REFINER
AND NATURAL GASOLINE MANUFACTURER

June, 1936
Vol. 15, No. 6

A Gulf Publishing Company Publication
EDITED MONTHLY AT HOUSTON, TEXAS

Copyright, 1936

GEORGE REID
Editor

CONTENTS

Fundamentals of Solvent Refining 199
John M. Poole

The Solvent Dewaxing Process 205
W. P. Gee, W. Kiersted and B. Y. McCarty

Propane De-asphalting and Dewaxing of Mid-Continent Residuum 210
A. P. Anderson, H. O. Forrest and Lee Van Horn

Color Restoration of Gasoline and Kerosene in the Field 217
J. B. Rather and L. C. Beard, Jr.

Clay Treating of Motor Fuels 219
M. R. Mandelbaum and P. F. Swenson

Instrumentation in Oil Refining 225
A. C. Proctor and Gustav Egloff

Controlled Disposal of Wastes vs. Pollution 232
W. B. Hart

Natural Trends 236
T. W. Legatski

Methods of Expressing the Volatility of Motor Gasoline 239
W. W. Scheuman

The Spectacular Side of Hydrocarbons 242
Sidney Born

Polymerization of Gases to Produce Gasoline 243
C. R. Wagner

Departments

The Look Box ..... 197 and 39a

Plant Activities 49a

Business Notes 52a

Ideas 56a

Science and Technology (Abstracts) 60a

New Equipment for the Modern Plant 73a

Catalogs and Bulletins 76a

Advertisers' Index 78a

SPECIALIZED OIL JOURNALS

Published by

GULF PUBLISHING COMPANY

OFFICE OF PUBLICATION
3301 Buffalo Drive, Houston, Texas

R. L. DUDLEY, *President*
A. L. BURNS, *Gen'l Manager*
S. W. ROBINSON, *Editorial Director*
J. KENT RIDLEY, *Managing Editor*

NEW YORK: Room 1023, 250 Park Avenue, Dick Swinsky, Manager.

PITTSBURGH: 902 Standard Life Building, W. W. Pigue, Manager.

CHICAGO: Room 1834, 332 So. Michigan Ave., T. W. Nelson, Manager.

LOS ANGELES: 416 Haas Building, W. E. Green, Manager.

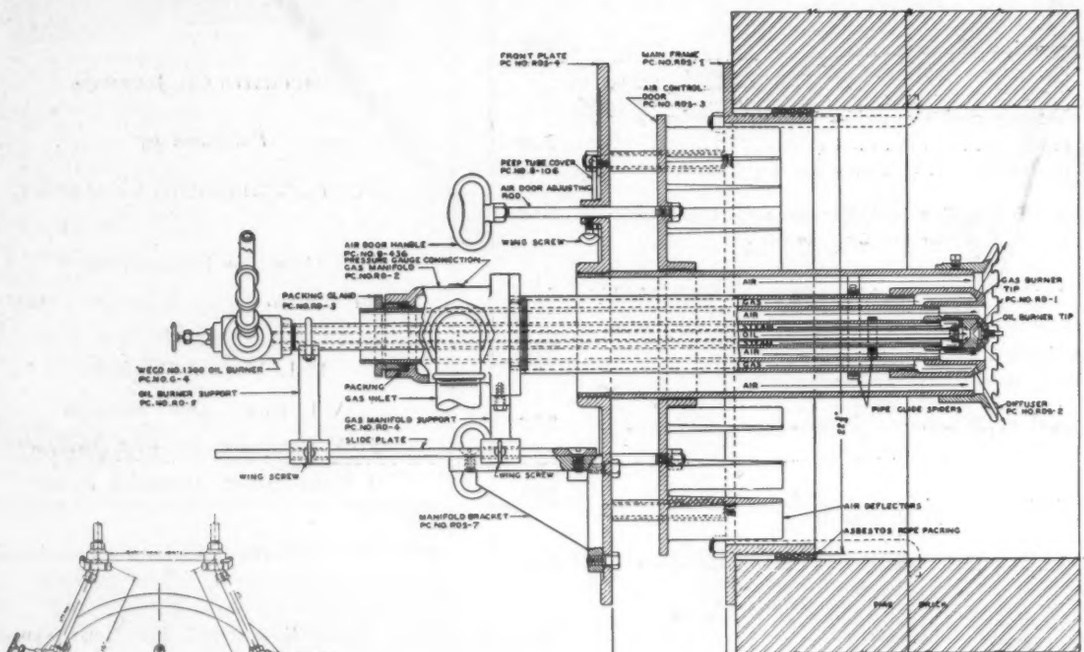
TULSA: 1513 Hunt Building, J. F. Carter, Jr., Manager.

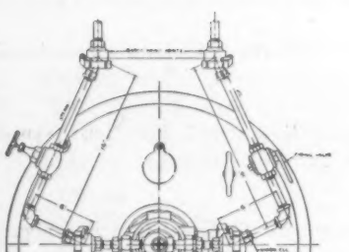
FORT WORTH: 203 W. T. Waggoner Building, H. H. King, Manager.

Single copies 20 cents. Domestic subscription price $1.00 a year. Canada and Foreign subscription price $2.00 a year. Entered as second class matter June 16, 1923, at the post office at Houston, Texas, under act of March 3, 1879. Advertising rates on application.

WEBSTER... ENGINEERED...

An installation of Webster Combustion equipment assures, First: That the equipment itself is properly engineered to give entire satisfaction in the service for which it is designed. Second: That the actual installation is based on an accurate knowledge of the conditions under which the equipment is to operate.





The RD SERIES BURNER is designed primarily for burning all types of refinery fuels with a high type of combustion. Burner is adjustable so that flame pattern can be changed to suit furnace requirements—precision control of temperatures. The same heat pattern is obtained with oil fuel as with gas.

Every WEBSTER INSTALLATION is GUARANTEED to give entire satisfaction.

THE WEBSTER ENGINEERING COMPANY

Tulsa, Oklahoma

Division of

THE SURFACE COMBUSTION CORPORATION TOLEDO, OHIO

VOLUME 15, No. 6 JUNE, 1936

REFINER
AND NATURAL GASOLINE MANUFACTURER

A GULF PUBLISHING COMPANY PUBLICATION

The Look Box

AS has been customary for the past few years at the time of the meetings of the Division of Refining at the conventions of the American Petroleum Institute, THE REFINER again presents all of the technical and engineering papers presented at the recent mid-year meeting of the Institute at Tulsa. At each meeting of the Refining Division of the institute three full sessions are devoted to technical and engineering progress reports and each year these programs become more interesting, more valuable, and hence more important to those within the industry who are concerned with its progress and its rapid technical development. The same is true of the annual meetings of the Natural Gasoline Association of America, and for this reason three of the discussions presented before that group last month in Tulsa are included in the technical section of this issue.

Technical Papers

Because of the importance of the studies before these conventions the editors feel it incumbent upon them to give its readers as much as possible of the engineering and technical information coming out of these important conferences in the issue of current date with the meeting. This policy, upon which THE REFINER has been complimented many times, assures those engaged in the industry that they will receive all of the important technical information presented at the meeting under one cover and at an early date following the meetings.

Bringing together the timely papers presented before both of the conventions held at Tulsa in May forms an especially strong technical issue of this journal. There are three papers devoted to the use of solvents in lubricating oil manufacture. These are presented under the titles "Fundamentals of Solvent Refining," "The Solvent Dewaxing Process," and "De-Asphalting and Dewaxing of Mid-Continent Residuum by Use of Propane." For those who have been requesting up-to-the-minute information on progress in the solvent field, these papers will prove of especial interest and value. The paper "Clay Treating of Motor Fuels" correlates a deal of technical information in this field and brings the experience record down to date. Another correlation of important, modern information of timely interest is the paper on "Instrumentation in Oil Refining." Additional papers from the Division of Refining Program presented in this issue include "Color Restoration of Gasoline and Kerosene in the Field" and "Controlled Disposal of Waste vs. Pollution."

From the program of the Natural Gasoline Association of America, the papers selected for publication here include "Natural Trends," an important economic-technical type of study which should be interesting to both refiners and gasoline manufacturers. "The Spectacular Side of Hydrocarbons" will prove a most thought provoking discussion. The paper "Methods of Expressing Volatility of Motor Gasoline," as a

correlation of information and engineering data on this increasingly important subject of "volatility index" is most useful. A timely paper on the production of gasoline from refinery gas by one of the commercial polymerization processes is included in this issue, coming from a recent meeting of a technical group in Pennsylvania.

Rodessa Crude

CRUDE from the Rodessa field of Northwestern Louisiana and Northeastern Texas going into refineries at the rate of 50,000 to 60,000 barrels daily at present is presenting something of a problem in many instances. The chief problem is that of octane rating. The crude yields, according to Bureau of Mines analysis, 32 percent of gasoline and naphtha and 20 percent kerosene distillate, with a fair yield of lubricating oil distillate, gas oil and bottoms. It is classified as a paraffin-base crude, with sulfur percentage of 0.18, pour point of 25° F., dark green color, and A. P. I. gravity of around 43 degrees. Plant operations, however, secure a gasoline yield of around 30 percent of 357/400 end point and with an octane rating of 42-44.

The low-octane rating of this motor fuel is not conducive to profitable skimming plant operation, nor for cracking and reforming operation with any but the best of modern facilities. Skimming plants now processing this crude are apparently cutting deep into the crude for maximum yield of a motor fuel now generally classed or termed as "Rodessa no-octane." The possibilities of making more profit in skimming through production of special naphthas from this crude are not so good. Chiefly for the reason that Michigan operators are specializing in this field and have freight rate advantages, not much has been attempted by Rodessa operators in this market.

The refineries not equipped with modern cracking facilities or reforming units, or both, are not over enthusiastic about the possibility of processing the crude. Cracking units installed 10 to 12 years ago were not designed for operation at the pressures and temperatures necessary to secure maximum yield of high-octane motor fuel from this type of crude. Yet to process Rodessa distillates and bottoms successfully it is apparently true that both cracking and reforming may be necessary.

These conditions point to the installation of more cracking and reforming or combination processes. Already two refineries in North Louisiana are erecting cracking units for processing Rodessa crude. One plant will take out the lubricating oil fraction for further processing. It is reported that still other refineries at Shreveport and Baton Rouge will soon start programs of construction involving installation of modern cracking or combination skimming-cracking-reforming processes. Some attribute such construction solely to the necessity of preparing for the treatment of Rodessa oil, but it must be remembered that refineries in Louisiana and Arkansas have been doing but little modernization work, especially in cracking, during the past several years. Many of the cracking units in the area are hoary with age, as cracking unit age goes. Possibly the presence of such a crude and the necessity for processing it has accelerated decision to proceed with modernization programs, and to that end refinery management may deem Rodessa a blessing. Much of the work now proposed or under way in this area would no doubt have been undertaken earlier had it not been for the proposed processing tax threat of a year or so ago.

There is little information available as to just how refractory the Rodessa distillates, topped crude, or heavy naphthas become when subjected to cracking conditions. It is reported however, that it is refractory and that older equipment can not handle it efficiently or safely. Further, some commentators state that the lead susceptibility of the gasoline is not good. Still further evidence of the lack of quality of the straight-run motor fuel now being produced by skimming plants is the fact that this third grade, "Rodessa no-octane", is selling at about a half-cent lower than East Texas third grade.

It appears then, that Rodessa should not become a hot bed of small skimming plants and that larger refineries will require the best of modern facilities to process this crude profitably.

Talco Crude

ANOTHER Texas field is in the making which will apparently produce a crude petroleum not too well suited to the desires and needs of refineries enjoying of recent years crude oils that are sweet and yield relatively high percentages of easily produced motor fuel. Estimates on the probable oil recovery from the Paluxy sand zone underlying the Talco faulted structure on the north rim of the East Texas Woodbine belt and near Mount Pleasant, Texas, range beyond the 100,000,000 mark. Appraisals placed on this area allow for about 7000 productive acres, extending in a general east-west direction. Apparently the field is around 4½ miles long but with subsurface data supporting forecasts of the field being eventually 7 miles in length with a width varying from a "shoestring" to 1½ miles. Early predictions on average recovery per acre range upwards from 15,000 barrels.

(*Continued on page 39a*)

The Fundamentals of

Solvent Refining of Petroleum Substances

JOHN W. POOLE
Consulting Technologist, Scotch Plains, N. J.

THIS paper has not been compiled for the purpose of describing any recent and important discovery in the art of solvent refining. Its purpose is, rather, to provide in as simple a manner as possible an exposition of certain basic principles which everyone concerned with the operation of commercial extraction processes must keep in mind. It is written primarily for the petroleum engineer and technologist whose field of activity has been principally elsewhere—although, even as the writer has profited by actually putting these simple basic principles in ink, so may others, who are sophisticated in the art, profit by a review of facts which subconsciously they recognize.

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Mayo Hotel, Tulsa, May 14, 1936.

PHYSICAL CHEMISTRY AS IT RELATES TO SOLVENT REFINING

BY AND LARGE, he who is concerned with technology involving solutions of which both solvent and solute are liquids will deal almost exclusively with organic substances. Petroleum refining is no exception; and in the comparatively new art of solvent refining of lubricating stocks the field, as heretofore, continues to be one for organic and physical chemistry—or possibly better—for organic physical chemistry.

As in other branches of organic chemistry, that portion which merges with the more general aspects of physics has not been reduced to a point even remotely approaching the definite knowledge which we possess in the inorganic field. Within comparatively recent years our knowledge of inorganic, ionized solutions has become codified, and reduced to a comparatively small number of broad principles which, if not supplying the entire story, come vastly closer to so doing than is possible for organic solutions.

Therefore, at the present state of our knowledge, we may now turn to a few mathematical formulas and produce therefrom a deductive treatise whereby may be described the actions of such solvent effects as take place in a modern extraction plant for the production of superior lubricants. The writer believes that it will be most clearly understood by all if these effects are described by direct illustration; and, starting at the beginning, let us first suppose that in two separate utensils we possess quantities of two pure liquid substances, and that we refer to one liquid as "A" and to the other as "B."

In general, temperature permitting, the following sequence of events can take place: We shall first regard "A" as the "solvent" or substance in which another substance is to be dissolved; and "B," the "solute," the material which is to be dissolved in or dispersed throughout the solvent "A."

If "B" is slowly poured into "A," which is meanwhile well agitated to produce intimate contact, it will be found that for some time "A" will remain clear and bright with no evidence of a second coexisting phase. Eventually, however, "A" will become saturated with "B," and the addition of further "B" will cause the solution to appear murky as an incipient second phase appears. If we add more "B," there will be no further increase in the volume of the "A" phase, but all additional "B" will go to increase the volume of the newly-formed "B" phase. Actually, there will be a decrease in the volume of the "A" phase, for the following reasons:

If originally we had chosen to pour "A" into "B" instead of vice versa, the entire above description would still have been exact, provided only that, in the description, the terms "A" and "B" were substituted for each other throughout. To be sure, the second phase would probably appear at different quantities of added solute, but otherwise there would be nothing to differentiate between the two procedures. This dual function of both fluids is a point which can easily be overlooked, although it is known to all who are possessed of a good general knowledge of physical chemistry: The fact that each substance may act—and usually does—as both solvent and solute frequently renders valueless any study which is predicated on the existence of one solvent only and one solute dissolved therein. This is especially true when a third substance soluble in either solvent is present. Careless thinking can also lead to incorrect *material* balances by forgetting that an excess of the presumed solute causes the arbitrarily-named "solvent phase" to decrease in volume by dissolving a portion of the solvent which, in consequence, reduces the amount of solvent available to dissolve the solute, which thereby is precipitated to join the

"solute phase," and carry with *it* as much solvent as is necessary to saturate the precipitated solute.

In the light of the above, it might appear offhand that the effect of adding a quantity of one of the substances would result in a complicated method of arriving at an exact calculation of the distribution of the two components between the respective phases, and procurable only by repeated corrections. However, the calculation is extremely simple if made on the

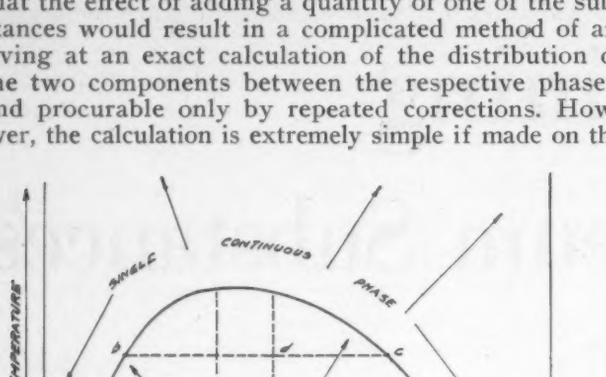


FIGURE 1

Phase Diagram for Two Hypothetical Liquids

basis of *total* quantities concerned. All that is necessary is a knowledge of the quantity of each substance necessary to provide a "saturated solution" in the other. This is an obviously simple determination. The algebraic formulas are as follows:

Allow: "A" to represent the total weight of the first component.
"B" to represent the total weight of the other.
P_1 = the weight of the first phase.
P_2 = the weight of the second phase.
a = the weight fraction of the first component of the first phase at the specified temperature *T*.
a′ = the weight fraction of the same component of the second phase at the same temperature.

Therefore, by material balance:

$$aP_1 + a'P_2 = \text{"A"}$$
$$(1 - a)\,P_1 + (1 - a')\,P_2 = \text{"B"}$$

If, for example, "A"= 500 lb., "B"= 250 lb., a = 0.20, and a′ = 0.90, substituting in the above equations would give the following solutions:

P_2 = 500 lb., P_1 = 250 lb. P_2 will consist of 450 lb. of the first component and 50 lb. of the second. P_1 will consist of 50 lb. of the first and 200 lb. of the second.

If the system is augmented by the addition of a quantity of either of the two substances, the simplest way to determine the nature of the change is to repeat the above calculation using the new totals for "A" and "B," and merely compare results.

For most two-component systems the above discussion applies over a considerable range of temperature. The saturation figures will, however, vary with temperature; and, in general, as the temperature increases, more and more of each constituent becomes soluble in the other until the two quantities coincide at what is sometimes called the "critical solution temperature." The point of coincidence for one pair of compounds will, in general, have no relationship—either as to ratios or temperature—to the analogous point for another pair of compounds. Above the "critical solution temperature," the two constituents are miscible in all proportions, and only a single phase can exist regardless of the relative percentages.

Figure 1, the phase diagram for two hypothetical liquids "A" and "B," illustrates in a concise manner the typical behavior of binary systems as just discussed. The two points marked respectively **a** and **a′** show how, at the temperature in question, the two phases will respectively contain 90 percent and 20 percent of "**A**." Abscissa **X** stipulates that "A" and "B" are present in the ratio of 500 pounds to 250 pounds (66-2/3 and 33-1/3 percent).

We have now seen how any two "pure" fluids which are not completely miscible each with the other can form two different types of solutions; and how, over a certain range of relative proportions and range of temperatures, the contacting of these two materials will result in the formation of two distinct fluid phases, each of which will comprise a portion of each constituent.

DISTILLATION OF BINARY SYSTEMS

The effects within these ranges, both of which are described graphically in Figure 1, are in general but little influenced by pressure—except when, by virtue of the existing temperature, the vapor pressure of the solutions tends to exceed the imposed pressure. In such a case vaporization will, of course, occur; the unvaporized portion will continue to obey the phase diagram even if heating is continued, while the vapor will obey the "laws" of vaporized binary solutions—a matter somewhat beyond the scope of these discussions and which, therefore, will not be considered in complete detail, although there is one angle of vaporization which is within the scope of our present interests: If two phases do co-exist at equilibrium and the imposed pressure is so established as to permit boiling to occur as soon as additional heat is supplied, either phase can boil—and even if the two phases should be removed to separate stills, the initial boiling point will be the same for both; and the first increment of distillate issuing from one will be identical with the first increment issuing from the other. A general statement of this fact is that the vapor pressure of any specific constituent is the same in all phases which co-exist at equilibrium. As a result of this, if two phases co-exist in a single still (for example, under conditions specified by point **d** in the phase diagram) boiling will take place at constant temperature **Tb,** and with unvariable distillate composition, until either points **b** or **c** are arrived at through the effect of preferential removal of one of the distillate materials. To be sure, if the composition of the distillate is identical with the abscissa **D,** or if as distillation continues an abscissa is attained which corresponds to the distillate composition, then evaporation will continue to dryness without ever attaining either of the points **b** or **c.** It is clearly evident that when still composition and distillate composition are identical no desirable function is performed by distilling equipment; and it is a good rule of thumb to state that, in distillation operations, two co-existing phases should be decanted as soon as possible.

An effect which is more or less a corollary of the above is that when "A" is the more volatile of the two constituents and boiling starts at **b** with only a single phase present, essentially the same phenomenon will be observed: i. e., boiling will take place at constant temperature and constant distillate composition, either until point **c** is attained or the charge

has been distilled to dryness. This means that while one phase alone may be charged to a still, a batch distillation will actually take place with two phases present. When the mechanism of the occurrence is studied, the reason for this fact is easily evident: "A" being the more volatile, the distillate will be richer in it than was the liquid from which it was removed; this is, in effect, to increase the relative ratio of "B" to "A" in the undistilled portion or to move the operation along line **b-d-c** to the right. Along this line we have already seen that the outward characteristics of vaporization are constant. In petroleum work, where a single fluid solvent is used, these various boiling and vapor-pressure characteristics may have little more than academic interest. However, for extraction with two solvents, or where a third fluid like steam is introduced for stripping purposes, these vapor-pressure characteristics may become highly important in the design and operation of solvent-recovery systems—so that a general knowledge of their nature is most desirable. Often when two phases tend to form under distilling or rectifying conditions, two separate stills or columns are necessary for efficient operation; and the feed for one will consist of a second phase which results from the operation of the other. For a more comprehensive consideration of the procedure and theory. The reader is referred to the *Principles of Chemical Engineering*, by Walker, Lewis, and MacAdams, McGraw-Hill Book Company. In some future paper, it is possible that the writer will discuss a specific case of two-phase distillation, involving the formation of a constant-boiling mixture; and show how, instead of proving to be an extremely expensive obstacle, such a happening can be utilized as an aid for simpler and cheaper operation.

MULTI-COMPONENT SYSTEMS

Up to the present we have been concerned with the matters pertaining to equilibrium between binary two-phase systems. The principles discussed involve no physical or chemical effects which result in the purification of a substance or substances. In fact, all that has been discussed so far is the vehicle by means of which refining can take place: Solvent-refining methods make use of a two-phase system by so controlling the conditions thereon that the *two separate phases* will behave like *two separate receptacles.* If the system is a suitable one, each phase will possess peculiar powers to hold within itself one class of material, while the other phase will possess an analogous power to collect and hold a different type of material. If originally these two types of material were mixed together, and one was an undesirable adulterant of the other—such as a sludge-forming compound in lubricating oil—it is possible to separate the undesirable from the desirable material by introducing the impure mixture into a two-phase system. This mixture will there be subjected to the preferential action of each phase to gather to itself one or the other of the two types of materials. In extractive refining for the production of superior lubricants, the so-called "solvent phase" tends to retain or extract the undesirable material and to reject the substances which comprise fine lubricating oils. The other phase, commonly referred to as the oil or "raffinate," tends to reject the undesirables while retaining substances of "paraffinic" nature. In actual operation, pains are necessary only to produce the solvent phase—since the oil phase will be automatically formed principally by constituents of the charge itself.

At this point many of my readers will presumably begin to wonder just why it is necessary to build up a rather unusual visualization of the process of extraction. To many it undoubtedly appears more logical to look upon the process as one in which undesirable materials are removed from a raw stock merely by exposing the raw stock to a solvent which will *dissolve* "undesirables" while desirable components are comparatively insoluble. The answer is this: The problem can neither be explained nor comprehended on the basis of "solubilities" alone! In fact, even the most logical analysis based on such a false premise is almost sure to be misleading, as is exemplified by a certain foreign patent which has been widely read and has deeply influenced "theory," but actually is productive of results entirely opposite to the avowed purpose of the patentees. Solubility is of importance, but of secondary importance only. The prime consideration in the determination of the effectiveness of any solvent process and the method of flow utilized therein is "distribution ratio."

Distribution ratio of a substance is defined as the concentration of that substance in one phase divided by the concentration of the same substance in another phase. Suppose, for example, that we have a two-phase system composed of crotonaldehyde and a petroleum residuum, in which the solvent forms the bulk of one phase and desirable lubricants the bulk of the other. In addition to crotonaldehyde and good lubricating oil, there will also be present within the system a considerable quantity of hydrocarbon material which is susceptible of oxidation with the resultant formation of sludge. This material will be distributed between the two phases in a ratio established by physico-chemical laws: Possibly every 1000 grams of "solvent phase" will comprise 200 grams of this sludge-forming material; at the same time, the "oil phase" may include 50 grams of the same sludge-forming substance for every 1000 grams of total substance. The distribution ratio of sludge-forming hydrocarbons, between the solvent phase and the oil phase, is, therefore, 200 divided by 50, which equals 4. The minor importance of solubility is illustrated by the fact that this sludge-forming material will, in all probability, be completely miscible in all proportions with both crotonaldehyde and the superior lubricating oil of which the latter forms the major portion of the oil phase. Generally speaking, the only necessary prerequisites regarding solubility which must be met by a satisfactory extractive solvent are: that undesirables are highly soluble in it; that "paraffinic" hydrocarbons are very sparingly soluble; and that it, itself, will not dissolve very greatly in liquid "paraffinic" hydrocarbons.

In a manner similar to that used for the sludge-forming hydrocarbons, a distribution ratio may be derived for all other constituents of the system. In the case of the solvent and "paraffinic" oils, however, this ratio will not be completely rigid: Both of these components are sparingly soluble in each other, and a distribution ratio is not a device whereby super-saturated solutions may be formed. Regardless of what the concentration would be when calculated by a predetermined distribution ratio, a *saturated* solution is the most concentrated which

can possibly exist. In consequence, since throughout an extraction operation the solvent phase generally is saturated with paraffinic oil and the oil phase is saturated with solvent, material balances and other calculations involving these components are best handled on the basis of absolute solubility; furthermore, from one stage to another, the variation of either saturation figure is small and of comparatively little concern. In the end of the system from which the spent solvent is expelled, the concentration of paraffinic constituents is, to be sure, highly important from the viewpoint of yield. However, that is a rather long and complicated question, and capable in itself of supplying ample material for a separate paper. Furthermore, it is a question more of an operative refinement than of basic principles *per se,*

As one travels from one end to the other of a counter-current extraction system, the distribution ratio of undesirable constituents between phases will not remain entirely constant. Of course, if only three pure components were present, the distribution ratio for one of them which chanced to be completely miscible with the other two would, over a considerable range of conditions, remain but little changed. For example, if into a two-phase system we should introduce 500 grams of a pure substance, miscible with both phases, and the distribution was found to be 400 grams and 100 grams, respectively, it would be reasonable to expect that 1000 grams would divide in about the same ratio or, roughly, 800 grams to 200 grams.

In making the above statement, it is pre-supposed that we are discussing moderately dilute solutions containing three pure components. With the commercial solutions encountered in solvent refining, the undesirable hydrocarbon substances are far from pure; in fact, they comprise a multitude of individual compounds, each of which has its *own* individual distribution ratio. Any ratio which is calculated on the basis of the entire extract is ,therefore, a composite figure—a species of *average* distribution ratio. Since those components of the extract which have a high ratio between the solvent and oil phases will be the more readily removed and quickly travel toward the solvent exit, the "distribution ratio of the extract" will steadily decrease as the oil phase passes on from stage to stage. It is impossible, therefore, to simplify the problem by calculation of a multi-stage extraction on the basis of a constant distribution ratio. Only over short portions of the line of flow can any specific ratio be used with reasonably quantitative accuracy; but, for purposes of visualization, it is necessary—and, I might almost say, it is sufficient—to bestow upon "distribution ratio" qualitative significance. It is only in the light of such visualization that the great value of counter-current flow is made evident. It is through intelligent application of this principle that most manipulative improvements have come about, whereas failure to recognize its import has cost great sums in wasted efforts. It is, in short, *the* basic principle of solvent extraction.

THE TWO VARIETIES OF SOLVENT REFINING

In the preliminary discussion of the two hypothetical components "A" and "B," it was observed that at temperature **T** two phases will co-exist over 70 percent of the compositional range. The point has been made that such a two-component two-phase system does not represent a process capable of refining action, but merely a vehicle *by means of which* refining can be effected—if and when a raw charge is introduced into the system.

To provide a less abstract illustration, let us say, for the time being, that "A" is phenol and "B" is a highly "paraffinic" lubricating oil—which, for purposes of momentary illustration only, may justly be regarded as a pure substance. From Figure 1 it will be seen that at the temperature of line **a-a′**, two phases can be made to appear under two separate conditions: (1) when enough lubricating oil has been poured into phenol to give a ratio of 10 parts of oil to 90 parts of phenol; or (2) when enough phenol has been poured into oil to provide a ratio of 20 parts of phenol to 80 parts of oil. If the proportions of phenol and oil are so intermediately established that *both* of these saturated phases will be present in sizable proportions, the system can serve as a suitable *mechanism* for that variety of solvent refining which has heretofore been briefly discussed. Upon introducing a petroleum substance which comprises an undesirable "naphthenic" material, as well as a large amount of the same fine "paraffinic" oil, "B," the "paraffinic" oil will join this oil phase, but the "naphthenic" portion will become a part of the solvent phase—and a separation of the two constituents of the raw stock thus be effected. The separation is to be sure, not quantitative, but even in this single-stage operation will be substantial; the principle involved is amply illustrated without discussing the technology necessary to produce commercially quantitative separation. Since it has become customary to observe refining operations objectively, with respect to "impurities" removed, the above operation, in which oil impurities become dissolved in the solvent is representative of "solvent extraction" of a petroleum substance, and must not be confused with solvent-refining methods which operate on an entirely different principle.

To illustrate this second type of refining, we may also use Figure 1, although we must partially redefine it. We will still retain component "B" and continue to designate it as high-grade "paraffinic" lubricating oil. However, for "A," exemplified by phenol, we shall substitute a solvent "A‴" which behaves somewhat differently from phenol. Liquefied propane is representative of this type. All solvents which are highly effective as dewaxing agents also come within the category.

These solvents are used only within that area which is denoted as "single continuous phase," as contrasted to the previous type which is used solely within the "two-phase region." Such solvents as "liquefied" propane are, in fact, generally used at a temperature so high that, regardless of the relative proportions of "A‴" and "B." two phases cannot co-exist in a system of pure "A‴" and pure "B" alone; in other words, the two basic components are usually miscible in all proportions at the temperature of use. The vehicle for this type of operation is, therefore, a system which is described by some point within the "single continuous phase." Usually this point is one well to the left of the 50-50 point, being much richer in the solvent "A‴" than in oil "B."

Having established such a system to serve as a vehicle for refining, it will operate as follows: Introduce an increment of material, positively identical with the other increment of "paraffinic" oil and "naphthenic" impurities which we have just "re-

fined" by means of a phenolic two-phase extractive system. One thing only will happen: The entire increment, "naphthenic" and "paraffinic" constituents alike, will merge with the single continuous phase. There will still be only the one homogeneous body of material, and no worthwhile service will be performed. The point is that "naphthenic," as well as "paraffinic," substances are completely miscible in all proportions with solvent "A'"; and, for removal, require a two-phase extractive system. In the use of the word "naphthenic," I am subscribing to the regrettably inaccurate use of the term to describe such undesirable matter as is removed by an extractive solvent such as phenol, crotonaldehyde, furfural, and the like. Such extracted material is characterized by its unusual affinity for other organic liquids; any solvent highly miscible with "paraffinic" bodies will assuredly be miscible with "naphthenic" substances of equivalent boiling point, and frequently will continue to be highly miscible with the latter—even if means are employed which render the "paraffinic" substances practically non-miscible.

The above discussion may appear to be an overthorough treatment of a non-existent refining operation, but I do wish strongly to impress the fact that such solvents as propane and dewaxing agents are totally different in their action from normal extractive solvents. To be sure, it may be logically argued that if the temperature is so lowered that the operation takes place in the two-phase region, a class "A'" solvent may serve in an extractive capacity: Qualitatively, this statement is often true, and operation then becomes similar—as proved by experiment—to the extractive procedure previously described. On the other hand, the nature of the phase diagram is usually such that the distribution ratio of the "naphthenic" material is not advantageous, and an extractive operation is, in consequence, commercially nonfeasible.

But even if not suitable to performing all types of separations, the single continuous phase can be effective within the proper field of use—and solvents of the class "A'" type will produce fractionations of a useful nature. If a material is at hand which contains "paraffinic" lubricating oil "B" and, in addition, certain heavy asphaltic bodies which are even less miscible with organic liquids as a whole than is "B," we may introduce such material into a proper single-phase system and separate the asphalt from the desirable lubricant. When an increment of such raw stock is added, the bulk of the "paraffinic" material will merge with the single-phase system; the asphaltic matter, however, will be substantially rejected, and will not even be permitted to enter the system. A separation of the raw stock into different classes of material is thus brought about.

The above presentation is not submitted as the one and only basis for description of and differentiation between the two major varieties of solvent refining of petroleum. Nothing more is claimed than that it constitutes the concept which, after 10 years' interest in solvent refining, the writer finds to be the most helpful to him in studying such problems and, in his experience, the most consistent with facts. The writer would not say that he "disagrees" with those who choose to call an "extractive" solvent a "solvent for naphthenic and aromatic hydrocarbons," and solvents such as propane "solvents for paraffinic hydrocarbons." It is merely suggested that, since one of the latter type is, under normal conditions, even a better solvent for "aromatic and naphthenic" hydrocarbons than for "paraffinic" hydrocarbons, such nomenclature may be misleading even to capable technologists who chance not to be highly skilled in this particular art. Personally, the writer—looking at the problem objectively from the viewpoint of "impurities" to be removed from high-grade lubricating oil—prefers the terms "extractive" and "precipitative" solvents, respectively.

OTHER NOTEWORTHY FACTS CONCERNING PRECIPITATIVE SOLVENTS

While it is admittedly possible to regard precipitative solvents as "solvents for paraffinic" hydrocarbons, the statement must be qualified by adding —*"under proper conditions."* One "proper condition" is that the "paraffinic" substance be present as a potential fluid: i. e., the substance is one which normally melts at a temperature lower than that which exists in the system. In passing through the melting point, a radical change in miscibility takes place—and below this point the tendency of petroleum substances to be miscible with solvents is, in general, greatly reduced—frequently changing from the category of complete miscibility to a saturation value of a fraction of 1 percent. These so-called "solvents," if added under favorable conditions of solvent-oil ratio and temperature, result in the precipitation of certain substances which form a second phase, which is not necessarily homogeneous in nature. The precipitated substances may be of two distinct types—petroleum waxes and/or asphaltic material. The mechanisms involved are—lacking more comprehensive research on fundamentals—somewhat debatable. Offhand, it would appear logical to suppose that the addition of the solvent brought about a precipitative or salting-out" effect, whereby the power of the paraffinic components to dissolve asphaltic substances became decreased. Possibly this may be a partial explanation—although the writer, even if unwilling as yet to be dogmatic, is reasonably well convinced that most, if not all, of the consequences are due to the phenomenon first described: In the writer's belief, the "precipitate" from such operations is fundamentally composed of substances which exist at the temperature of operation as potential *solids;* propane precipitation of asphalt, and naphtha dewaxing, are mechanically similar phenomena. By the addition of a highly-miscible and fluid "solvent" of low specific gravity, the medium through which particles must travel is greatly reduced in viscosity; while at the same time an increased difference in gravity of the phases is brought about. By virtue of this double effect, separations can be accomplished which were theretofore mechanically impossible. When all the facts are "in," the writer believes that this *mechanical* theory as opposed to a *chemical* theory will be the answer. At the present time many data exist which tend to confirm the mechanical theory.

To a few able investigators, the fluid nature of certain of the precipitates may appear to contradict the above theory. In the author's opinion, these substances are not true fluids, but plastics or "muds" in which the potentially solid material plays the same part as clay does in ordinary mud; while truly fluid hydrocarbons, which are constrained by the solids, act as plasticizers. Some day, when there is much less work to do on extractive solvents, or when the

writer has greatly increased facilities at his disposal. he hopes to settle these points definitely.

THE FUNCTIONS OF SOLVENT PROCESSES

Precipitative solvents tend to remove from a raw stock the substances which melt at comparatively high temperature, a statement which amounts to saying that they tend to remove substances of high molecular weight or of moderate molecular weight and extremely great paraffinicity. In case there are those among my readers who are unconvinced as to the "mechanical" theory of precipitative solvents, the last statement is provided with further substantiation—which, although not used in substantiation of the "solids" argument, might well have been. By and large, distillation is a method by which comparatively heavy molecular substances may be separated from lighter molecular substances by throwing the latter overhead as distillate. If carried sufficiently far —using steam, high vacuum, or both—such distillations are roughly equivalent to "propane precipitation" of asphalt. Figure 2 is a graphical representation of how a petroleum fraction—for example, a residual stock—may be purified to produce a premium lubricating oil.

In this illustrative diagram, which is completely hypothetical, minor inconsistencies are permitted for simplification. Each small circle is representative of one volume, say one quart of residual stock. The location of each circle specifies the characteristics of that quart of oil. Those at the bottom are the least paraffinic; those at the top the most paraffinic; in fact, these are true paraffins, solid at normal atmospheric temperature. A circle at the extreme left of the diagram would boil at the lowest point of all; a circle at the extreme right would boil the highest. When all of these quarts of different types of hydrocarbons are mixed together, they constitute a hypothetical residual lubricating stock, produced by removing the naphtha and gas-oil fractions. If this constitutionally-complicated substance is subjected to conventional propane precipitation, a separation along line **a-b-c-d** will be brought about. Material to the right of this line will contain the high-melting and high-boiling asphalts—and the stock has now become "de-asphalted." De-asphalting can also be brought about by continued distillation—say, to line **e-f**; such a separation not, of course, being entirely identical with, but broadly approximating the results of the precipitative step.

For production of a premium lubricant there still remain two other types of substances to be separated from the remaining portion of the stock. Only such substances as lie within an area such as that which is cross-hatched in Figure 2 conform in all respects to requirements of high viscosity index, low carbon residue, and unusual stability. Such undesirable materials as have not been removed by the de-asphalting procedure and lie below the cross-hatched line may be substantially removed by a true extractive operation such as is possible by solvents like crotonaldehyde, nitrobenzene, "chlorex," or various phenolic substances. To be sure, such extraction may not be made to coincide exactly with the lower boundary of the "good-oil" area: Lower-boiling substances are inherently more soluble than are those boiling at higher temperatures, and a treatment which will be ideal for materials of average boiling point will slightly over-treat the low-boiling end and somewhat under-treat the high-boiling end. The relationship between the lower boundary line and line **h-j**, which is the "extraction" line, will illustrate this point. The extracted material is that which lies below line **h-j** and is characterized by poor viscosity

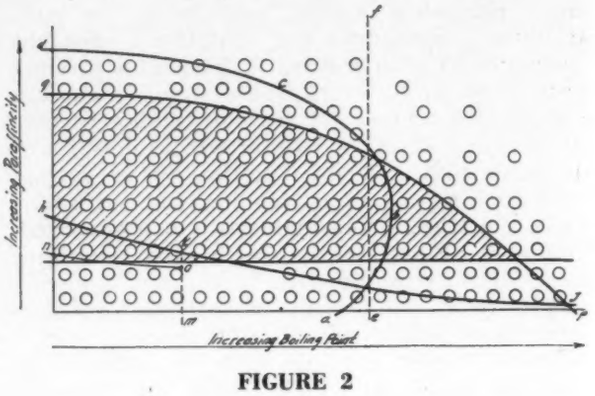


FIGURE 2

index, high carbon residue, lack of stability, high pigmentation, and generally represents a material which is undesirable for the average lubricant. The only materials which comprise it and possess much real value to lubricants are certain "polar" substances which do tend to cause an oil to stick better to bearings and thereby assist in maintaining a coating or film of lubricating oil.

In the lighter fraction of this extract there may exist a fair amount of material which could desirably be included in the final high-grade product. If it is considered worth the effort, a considerable percentage of such materials can be salvaged: If the extract is subjected to distillation, a high percentage of such material may be recovered—in a very impure state, to be sure—by collecting a distillate of, say, one-third of the extract. Such a distillation can be portrayed by a line **k-m.** The distillate will be the portion to the left of this line—which area, it will be seen, includes the bulk of the cross-hatched area included in the extract. This distillate may be accumulated and again extracted with a solvent of different solvent power from that previously used, for example along line **n-o**. The material above this line can be added back to the original raffinate.

The material above the cross-hatched area is undesirable from a single viewpoint only: Being substantially pure paraffins, it is composed of substances which are solid at normal atmospheric conditions and will tend to cause the oil to congeal and by inability to flow, to fail of proper lubrication. By modern dewaxing methods, it can be removed so efficiently that the line of demarcation of the two fractions will substantially coincide with the prolonged upper boundary **q-p** of the cross-hatched area. It will be noted that the steps which have been utilized in the refinement of the hypothetical residual stock, overlap, to a small degree; in consequence of which the several by-products will be influenced somewhat by the order of these steps. An oil dewaxed before de-asphalting will produce a "petrolatum," which may contain very considerable percentages of asphalt; and an oil which is extracted prior to de-asphalting will produce an extract containing appreciably more and harder asphalt. Since these extracts may invariably be reduced by distilla-

(Continued on page 209)

The Solvent Dewaxing Process . . .

W. P. GEE, W. KIERSTED, and B. Y. McCARTY
The Texas Company, New York

IN a paper entitled "Solvent Dewaxing of Oils with Benzol and Acetone," presented before the American Petroleum Institute, May 17-18, 1933, Govers and Bryant gave a general discussion of the operation of the solvent dewaxing process installed at the Lawrenceville, Illinois, refinery of Indian Refining Company. This installation was made in 1927, and was the first of its kind. The past three years have, in response to urgent demands from the industry, witnessed rapid and important progress in the development of commercial operating equipment. The purpose of this paper is briefly to review this development, to explain the reasons for the phenomenal expansion of the process to those not already familiar with its operation, and to point out the essential requisites of an economical dewaxing installation.

Public demand for low-pour-test oils of high viscosity index has brought refiners comparatively recently to the realization that the older methods of dewaxing must be replaced by a more efficient process—one that would fulfill the following requirements:

1. **Produce from waxy stocks the maximum yield of wax-free oil consistent with normal stock fluidity and having the desired pour point.**
2. **Be suitable for dewaxing any lubricating stock.**
3. **Permit switching from one stock to another with a minimum loss of time or contamination of products.**
4. **Be economical to operate.**
5. **Be low in initial cost.**
6. **Be flexible in design, so as to permit expansion of the plant to meet any increase in demand for products.**
7. **Be so advanced in fundamental theory as to obviate obsolescence, by providing a dewaxing system that will permit incorporating into existing plants processing improvements that may be evolved from research and the wide application of the process throughout the industry. All of these requirements are met by the solvent dewaxing process.**

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 15, 1936.

1. MAXIMUM YIELD OBTAINABLE

A MAXIMUM yield of dewaxed oil is insured by two fundamentally sound principles: 1, the use of a solvent which can be accurately controlled as to solvent power in order to permit complete separation between wax and oil solution; 2, the use of filtration to separate sharply by mechanical means the precipitated wax crystals from the chilled oil-solvent solution.

The process in its present commercial form employs a mixed solvent including an oil solvent, chemically related to the oil, which will retain the oil in complete solution at the dewaxing temperature but will not exert excessive solvent action upon the wax content; and a wax anti-solvent, chemically dissimilar to the oil, which will effectually eliminate any tendency of the wax to remain in solution at the dewaxing temperature. The wax anti-solvent, in addition to promoting crystal growth and wax precipitation, is also a material aid to filtration by reducing the viscosity of the oil solution.

Unfortunately for the industry, the solubility of different oils and different waxes is not the same. If this were the case, a single solvent possessed of sufficient selectivity to serve in itself as a solvent and anti-solvent might be suitable for all dewaxing purposes. Generally speaking, however, the higher the viscosity and the greater the so-called paraffinicity of an oil, the lower will be its solubility. The difficulty of securing a single solvent that will serve equally well for dewaxing all oils becomes at once apparent. A correct mixture of several solvents, on the other hand, permits a clean separation of oil solution from wax crystallized at any desired temperature of filtration.

Commercial 90-percent benzol is now used as the most suitable oil solvent due to its high solvent power for oil, low wax solubility, stability, and availability in commercial quantities at low cost. The ketones possess excellent properties as wax anti-solvents. Of these methylethylketone and acetone are the two wax anti-solvents now generally employed in commercial application of the process. Either can be used in any case, and the selection between the two is generally a matter of operating or investment economy.

The process is characterized by high yield of wax-free oil and low dewaxing differential (difference between dewaxing temperature and pour test). Plants now in operation dewaxing to 0°F. pour test demonstrate that the wax cake removed by filtration contains practically no 0°F. pour test oil. The practically complete separation of wax is accomplished, moreover, at a temperature substantially the same as the pour point of the dewaxed oil desired. Filters afford the fundamentally sound means of mechanically separating the wax-free oil solution from wax, since the wax cake when formed on the filter medium can be removed from the unfiltered solution, and any oil solution retained in the cake can be washed through to the filtrate system. High yield is of growing importance because of the tendency toward solvent refining, which increases the value of dewaxing-plant charge stocks.

The ability to produce the maximum yield of low-pour-test oil at a temperature substantially the same as the pour point has thus been commercially demonstrated.

2. DEWAXING STOCK

All types of stocks from gas oil to heavy residue have been successfully dewaxed on a commercial scale by the solvent dewaxing process. Table 1 is presented to illustrate some of the stocks handled in

TABLE 1

Solvent-Dewaxing Results

STOCK	Raw Light Coastal Distillate		Raw North Texas Residuum		Raw Oklahoma Residuum		Raw Pennsylvania Long Residuum		Raw Pennsylvania Distillate		Raw Kettleman Hills Distillate	
SOURCE	Coastal		Mid-continent		Mid-continent		Pennsylvania		Pennsylvania		California	
Solvent composition:												
Acetone, percent	....		....		....		....		....		50	
Benzol, percent	50		45		45		60		60		50	
Toluol, percent	....		....		....		....		....		....	
Methylethylketone, percent	50		55		55		40		40		....	
Yield of wax-free oil, percent	99.0		78.0		88.0		85.0		82.0		84.0	
Dewaxing temperature, °F	—40		+10		—12		—10		—10		—5	
TESTS:	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**
Gravity, A.P.I.	27.3	26.9	22.3	19.4	23.6	22.4	28.3	27.3	34.0	31.2	19.8	17.0
Flash point (Cleveland open cup), °F	280	290	545	540	440	450	435	420	290	365	435	430
Fire point (Cleveland open cup), °F	305	325	625	630	500	505	480	500	390	410	505	505
Viscosity, Saybolt Universal, at 100 °F	58	63	6,000	.....	1,200	1,644	590	730	80	107	1,050	2,500
Viscosity, Saybolt Universal, at 210 °F	.....	.....	271	300	90	102	74	76	38	40	74	95
Color	.....	.....	Dark	Dark	Dark	1 Tag-Robinson (Dilute)	Dark green	Dark green	9¾ Tag-Robinson	9 Tag-Robinson	Green	Green
Pour point, °F	—40	—55	+110	+15	+85	—5	+45	—5	70	0	110	0
Carbon residue, percent	0.01	0.02	6.0	6.4	3.0	2.65	1.40	1.42	0.01	0.03	1.70	2.1
Viscosity index (Dean and Davis)	.....	.....	.....	.....	81	73	113	98	.....	100	45	—14
Viscosity-gravity constant	0.864	0.864	0.831	0.852	0.840	0.847	0.809	0.815	0.813	0.824	0.875	0.892

STOCK	Petrolatum		Solvent-refined Oklahoma Residuum		Solvent-refined Mid-continent Distillate		Solvent-refined German Haenigsen Residuum		Solvent-refined Iraq Distillate		Solvent-refined Coastal Residuum	
SOURCE	Mid-continent		Mid-continent		Mid-continent		Germany		Persian-Iraq		Coastal	
Solvent composition:												
Acetone, percent	....		....		35		30		35		....	
Benzol, percent	60		50		52		65		65		60	
Toluol, percent	....		....		13		5		....		....	
Methylethylketone, percent	40		50		....		....		....		40	
Yield of wax-free oil, percent	50.0		82.0		84.0		82.0		78		96.0	
Dewaxing temperature, °F	—12		—10		—11		—12		—15		—5	
TESTS:	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**	**Charge Oil**	**Wax-free Oil**
Gravity, A. P. I.	28.4	23.9	28.4	28.2	28.1	27.3	27.4	25.9	31.1	29.3	25.4	25.3
Flash point (Cleveland open cup), °F	.....	485	545	530	495	495	475	475	385	375	455	460
Fire point (Cleveland open cup), °F	.....	575	600	590	570	565	530	530	420	425	540	530
Viscosity, Saybolt Universal, at 100 °F	.....	2,068	1,350	1,550	625	755	630	804	.....	176	1,265	1,272
Viscosity, Saybolt Universal, at 210 °F	87	118	107	109	67	72	72	77	44	45	92	91
Color	.....	¼ Tag-Robinson	Dark	Dark	40 (½ in. Lovibond)	27 (½ in. Lovibond)	10 Tag-Robinson (Dilute)	½ Tag-Robinson	1¾	1¼ Tag-Robinson	1½ Tag-Robinson	1½ Tag-Robinson
Pour point, °F	112	—5	+115	0	+110	—5	+110	0	+110	—5	+25	—5
Carbon residue, percent	.....	1.4	0.32	0.32	0.08	0.10	0.40	0.46	0.13	0.15	0.47	0.48
Viscosity index (Dean and Davis)	.....	77	99	90	85	82	102	91	.....	100	80	77
Viscosity-gravity constant	.....	0.832	0.800	0.801	0.813	0.817	0.816	0.818	0.808	0.819	0.826	0.827
Paraffin, percent	42.0											
Melting point of paraffin, °F	128											

commercial units. Suitability of the process to any type of wax-bearing oil is thus shown.

3. STOCKS CHANGED QUICKLY

Commercial operation has demonstrated that a minimum of time is lost, and no contamination of products need result, when switching from one stock to another. Dewaxing processes which involve slow chilling, or which for other reasons require the presence of a considerable amount of stock in process tankage or equipment, naturally require appreciable time to replace one stock with another. The solvent dewaxing process, however, being conducted as a continuous operation in which rapid and continuous chilling is desirable, permits the use of chillers, filters, process tankage, and solvent-recovery equipment having a minimum volumetric capacity, in which the total stock oil in the complete system can easily be reduced to two hours' supply. Complete displacement of all liquid in the dewaxing plant can, therefore, be accomplished quickly. It is possible to terminate a run on one stock, wash the system with solvent, and be on steam dewaxing of a dissimilar stock within a very few hours at the most. In the case of similar stocks, where cutting by viscosity can be permitted, the change-over can be made without any loss of time.

4. ECONOMICAL OPERATION

Improvements in design of equipment have been attended by reductions in operating cost. The cost of power for pumping is now lower due to material reductions in pressure drop through improved refrigeration and heat-transfer equipment. Heat, in the form of steam or fuel, that is required for recovery of solvent from the wax-free oil solution, has been reduced by the introduction of the principle of multiple-effect evaporation, and by the use of additional exchangers. Refrigeration requirements have been reduced by more complete and efficient recovery of refrigeration from filtrate solution and slack-wax mixture. A reduction in operating labor has been accomplished by additional control instruments, by the use of larger filters, and by more convenient arrangement of piping and auxiliaries. Solvent loss has been reduced from 0.2 percent to approximately 0.05 percent of solvent turnover. The rapidity with which solvent in the system is turned over has been increased from one turnover in 12 hours to one complete re-use of the solvent every 2 or 3 hours.

As a result of economies in plant operation the unit cost of dewaxing has been reduced more than 50 percent in the past three years.

5. PLANT INVESTMENT LOW

Plant investment costs are low due to the fact that no special equipment of any kind is required; operating pressures are low; no corrosive liquids are employed; solvent-to-oil ratios for dewaxing solutions are low; and plant design is so flexible as to permit utilization to the fullest extent of local conditions or facilities such as refrigeration, conventional chillers, process tanks, etc., that may be available. The arrangement of equipment follows no set standard, since space requirements are comparatively small and the necessary tankage, towers, buildings, etc., can be arranged to suit almost any local requirement. Recent improvements in design, already mentioned as effective in reducing operating costs, have also served to reduce construction costs as well.

6. ECONOMICAL EXPANSION OF PLANT POSSIBLE

Equipment employed by the solvent dewaxing process can be purchased in large or small units. Because of the wide range in equipment sizes and the more or less unit type of construction used, capacity requirements need not be anticipated far into the future. It is sufficient to provide only for meeting immediate demands; since, with nominal provisions for expansion, the plant can be easily extended when and if sales requirements demand additional production.

Filters are available having capacities to handle from 100 barrels to over 400 barrels per day of oil charge each. The capacity of double-pipe chillers ranges from approximately 75 barrels to 200 barrels per day each, depending on size and the amount of solution solvent to be chilled with the oil. Refrigeration machines are available in almost any size desired. It is of major importance when considering provisions for future requirements that the principal items of equipment are available as units that can be operated in parallel with similar units originally installed.

7. INSURANCE AGAINST OBSOLENCE

The vast amount of research work already conducted in conjunction with commercial plant development, together with a general acceptance by the industry, furnish a secure basis from which the solvent dewaxing process looks to the future with every assurance of retaining its place as the universal dewaxing process.

RECENT CHANGES IN PLANT DESIGN

Figure 1 presents a simplified flow diagram illustrating the flow of oil and solvent through a typical solvent dewaxing plant. The general flow and operation of the process were described in detail in the paper by Govers and Bryant, and consideration will be given here only to those points which have been changed in recent installations.

The original installation of the process by Indian Refining Company employed batch mixing in preparing the charge solution. All subsequent installations have been equipped with a continuous-mixing device. Just ahead of this mixer the oil and solvent streams, respectively, are controlled by means of a ratio-flow controller so as to insure a continuously-uniform solution. Dewaxing operations were smoothed out appreciably by this change.

A solution temperature of the order of 100° F. to 120° F. is all that is ordinarily required. Temperatures from 50° F. to 60° F. above the complete solution temperatures have been found desirable, however, in preparing certain oils for dewaxing. Both filter rates and yields can be improved when handling these oils, by heating the solution to a "super-solution" temperature, after which the combined charge may be immediately cooled. A steam heater installed in the charge line followed by a water-cooled aftercooler are the only additional pieces of equipment necessary to effect the initial heating and cooling operation.

The original installation of the process involved the use of two brine solutions at different temperatures for chilling the charge solution from exchangers. This chilling method has been replaced in all newer installations by direct ammonia-expansion

chilling, the ammonia being supplied by either absorption or compression machines. The final double-pipe chiller is automatically controlled to give the desired dewaxing temperature. Brine chilling is unnecessary, although an existing brine system may be used as a matter of investment economy.

Two types of filters have been applied to solvent-dewaxing operations, viz.: continuous drum-type vacuum filters, and rotating-leaf pressure filters. Improvements in the design and construction of both the rotating-leaf pressure filters and drum-type vacuum filters permit the use of insulated filter shells instead of requiring insulated cold rooms previously used for filter installation. This has not only reduced construction costs, but has also improved operating conditions.

Whereas the original pressure filters used in the Indian Refining Company installation have a filtering surface of only 360 square feet per filter, pressure filters now in use have a filtering surface of 800 square feet, materially reducing the number of separate filters required and correspondingly the operating labor. Continuous-vacuum filters used in dewaxing have 300 square feet to 500 square feet of filtering surface, or more, as desired.

Probably the greatest operating improvements in the process have been accomplished by completely re-designing the original solvent-recovery system as used by Indian Refining Company. In fact there are now several designs that may be used with equal success as far as recovery of solvent is concerned.

Based upon the use of exhaust steam-heated evaporators, 80 to 90 percent of the solvent can be recovered using exhaust steam furnished by steam-driven pumps and machinery. Figure 1 presents this type of recovery equipment, in which live steam is used to vaporize practically all of the solvent remaining in solution. The heated oil from the lowest tray contains approximately 0.5 percent of solvent, which is easily removed in the conventional steam-stripping column. Solvent is recovered from the slack-wax and solvent mixture in essentially the same way.

In cases where electricity or other forms of power can be used to better advantage than steam for driving pumps and machinery, multiple-effect evaporators are used. Live steam or fired heaters serve to vaporize a substantial part of the solvent at low pressure. These vapors, in turn, are used to vaporize solvent from the filtrate solution at atmospheric pressure.

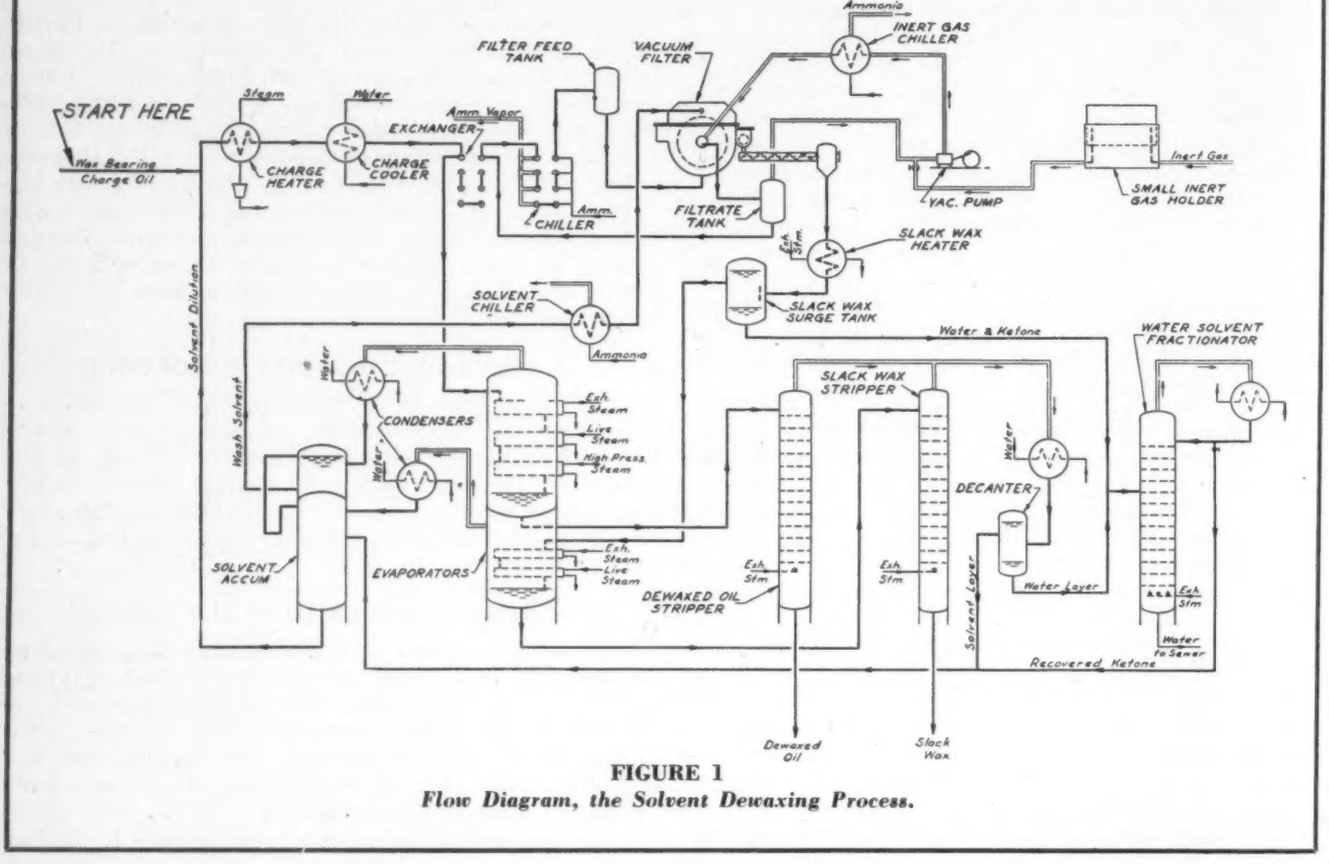


FIGURE 1

Flow Diagram, the Solvent Dewaxing Process.

The process, therefore, affords the designer wide latitude in selecting an economical basis for design. A careful study of the economics involved in each particular case is, accordingly, made before proceeding with plant design.

The original method of drying solvent by the use of soda ash is no longer employed.

The removal of water from the solvent is now accomplished by fractionation. Figure 1 illustrates how excess water, which may enter the system with oil charge from the steam-stripping operation or from condenser leaks, is removed. The following explanation will serve to clarify the solvent-drying operation.

Water present in the charge concentrates almost exclusively as ice in the wax cake. To separate the major portion of this water, the slack-wax mixture is heated by exchange and direct heat to approximately 200° F., and allowed to settle. The excess

water, containing solvent in solution, separates readily, and is withdrawn from the slack-wax settling and surge tank into a water accumulator for charge to the water fractionator.

Dry acetone or substantially dry methylethylketone is recovered from the water by direct fractionation as an overhead distillate. Water, free or solvent, is discharged to the sewer from the bottom of the tower.

The overhead distillate from a methylethylketone fractionator is a constant-boiling mixture of methylethylketone and water, containing 88.6 percent of methylethylketone by weight. On cooling to a temperature of 100° F., a small percentage of water solution separates out—increasing the percentage of ketone in the solvent layer to approximately 90 percent by weight. The separated water layer is recycled to the fractionator. Several methods could be used to remove the remaining water from the constant-boiling mixture; but the volume of constant-boiling mixture produced is so small in relation to the total solvent volume that additional separation is not necessary—and it is, accordingly, mixed with the main body of recovered solvent.

It will be seen from the above brief discussion that there is practically no difference in the recovery system when using either acetone and benzol or methylethylketone.

SOLVENT LOSSES

The solvents employed must, in the interest of economical operation, be stable at the temperatures required in the recovery process, easily recoverable from the oil, and not chemically reactive with the oil. Acetone, methylethylketone, benzol, and toluol have excellent qualities in all three respects as substantiated by records of solvent loss attending commercial operation of the process over long periods of time. This over-all loss, including losses due to leaks, spills resulting from occasional carelessness, and similarly avoidable causes, amounts to only 0.05 percent of the solvent turnover.

Precautions taken to keep losses to a minimum include the general use of welded lines and vessels, blanketing of solvent tanks with inert gas, and grease-sealed lantern glands on pump rods, chiller shafts, filter trunnions, and similar glands through which solvent leakage might occur.

The inert gas is furnished by a separately fired generator at an average rate not exceeding 20 cubic feet per minute. The inert gas, besides serving as a solvent blanketing medium, is circulated by a vacuum pump from the vacuum filtrate receiver through chillers to the filters to facilitate wax-cake discharge and cake drying. Any inert gas escaping to the atmosphere does so through an oil seal which absorbs solvent that may be present. This oil, and that used in the gas holder, is passed through the solvent-recovery system occasionally to reclaim the solvent held in solution.

CONCLUSION

Thus it is shown that the solvent dewaxing process fulfills the theoretical and practical needs of the modern refiner. The most impressive evidence of the success of the process is the acceptance accorded it by representative companies of the petroleum industry now licensees of the process.

The Fundamentals of Solvent Refining of Petroleum Substances

(Continued from page 204)

tion to produce asphaltic pitches of most excellent ductility, a refiner interested in producing asphalt of high ductility may find that extraction desirably comes first.

With reference to the matter of overlapping, there actually will exist "overlapping" of a type which cannot conveniently be shown by a diagram such as Figure 2. In actual operation, lines of separation may not be defined as clearly as indicated in the diagram. As here presented, one would conclude that the finished lubricant would contain all of certain substances, for example, a quart of oil centrally located in the cross-hatched area. Actually, none of the substances can be 100 percent diverted to any one fraction; but presumably all fractions (wax, asphalt extract, and finished lubricant) will contain at least minute portions from every circle shown. In the case of the lubricant, a few substances such as asphalt components may be present in minuscule proportions—especially if the lubricant has received a final processing, of a physico-chemical nature, capable of removing certain bodies practically quantitatively. The extract, however, will contain a little of everything which ever did exist in the raw residuum; in fact, the question of keeping the "paraffinic" content of extracts at a minimum is the most important operative problem of solvent extraction.

SUMMARY

The present exposition has covered only the bare foundations on which the technology of solvent extraction must be built. It should be kept in mind that there is a basic difference between fundamental principles and technological developments. The contents of this paper do not provide the information necessary to reproduce a process by means of which a specific stock may be refined. As a matter of fact, the variations in raw material are almost without end, and technology must be made to conform to each individual requirement. A truly comprehensive treatment, descriptive of actual processing details necessary to secure the best results on all types of stocks, would be encyclopaedic in size as well as purpose. As a broad objective, the writer has tried merely to describe clearly those factors with which technology must be in accord, and to depict those mechanisms which can be made to serve as tools but which may not be changed by the will of men. Specifically, the writer has hoped to establish clearly an appreciation of the difference between the basic principles and the utilities of "extractive" and "precipitative" solvents.

Propane

De-Asphalting and De-Waxing

of Mid-Continent Residuum

A. P. ANDERSON
Shell Petroleum Corporation, Wood River, Illinois

H. O. FORREST and LEE VAN HORN
The M. W. Kellogg Company, New York

THIS paper describes the design and operation of the propane de-asphalting and de-waxing plant at the Wood River refinery of Shell Petroleum Corporation. The plant represents the initial commercial application of de-asphalting, and also includes the novel feature of continuous pressure filtration. The process consists of mixing long residuum with about 4 volumes of propane, settling asphalt, and then removing about 2½ volumes of propane. The remaining solution is chilled by self-evaporation with addition of propane; cooled by exchange, to maintain concentration; and is then filtered to remove wax, and all products are de-propanized.

The plant has been operated at design capacity of 2450 barrels per day of dewaxed oil since chiller-foaming difficulty has been overcome. Initial difficulty of pumping the wax cake was solved by adding a small quantity of solvent to the cake in the wax conveyor.

Filter operation has been highly satisfactory, utilizing a pressure differential of about 4 pounds maintained by propane vapor, and filter rates of 3 gallons to 4 gallons of dewaxed oil per square foot have been realized.

Pour test of dewaxed oil is consistently —10°F., and subsequent solvent extraction and distillation produces cuts having pour points of 0°F. or below, and no cloud when held at +20° F. Average yields are about 78 percent de-asphalted and dewaxed oil, 3.5 percent asphalt, and 18.5 percent wax, with the unwashed cake containing about 30 percent of oil with reduction to 15-20 percent realizable with washing.

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 15, 1936.

THREE years ago the propane dewaxing process was first brought to the attention of petroleum refiners by the paper of Bahlke, Giles, and Adams' presented at the May meeting of the American Petroleum Institute. That paper discussed the preliminary experimental work on the process, and the design and operation of the propane dewaxing plant of Standard Oil Company (Indiana) at Wood River, Illinois. This original plant has been operated at and above capacity since that time, producing oils of —10°F. to —15°F. pour test, depending on the viscosity of the distillates processed.

During the interval, another plant of essentially the same type, with designed capacity of 1,750 barrels per day, has been built and put into successful commercial operation by Union Oil Company, at Oleum, California, for waxy California distillates.

It is the purpose of this paper to present the developments which led to the design of a plant for handling residual stock at Shell Petroleum Corporation's refinery at Wood River, together with a general description of the plant itself and a brief review of the operating results to date.

NEW DEVELOPMENTS

The two new developments which may be considered as largely responsible for the design of the Shell plant were continuous filtration and propane de-asphalting. Of course, the latter was not new in an experimental sense, but its application to commercial operation was new at the time this plant was conceived.

CONTINUOUS FILTRATION

In their paper Bahlke and his co-workers pointed out that: "Experiments being conducted at the present time indicate that a continuous process of filtration . . . can be readily developed to give results equally as good as, and probably better than, those described herein." They referred to a large amount of development work then being carried out by R. N. Giles and others at the Casper plant of Standard Oil Company (Indiana). The experiments were conducted on a 1-foot-diameter Oliver drum-type filter installed in a pressure vessel, with propane vapor used as a means of maintaining the pressure differential.

Since that paper was presented, the development work has been continued and a great deal of effort was spent in working out all of the problems involved in the operation of this type of equipment. It was believed to be entirely justified because of the axiomatic advantages of continuous operation of any apparatus as compared with batch operation. The problems of maintaining the pressure differential with propane vapor without rise in temperature and removal of the wax cake were satisfactorily solved in the pilot plant, and a great many experiments were made on a variety of stocks to show that continuous filtration was very flexible in its application. As a result of this extensive work, it was concluded during 1934 that the continuous filtration process was ready for commercial application.

DE-ASPHALTING

During this same period extensive work also was being carried out on the de-asphalting of various residual stocks. As Bray[2] and others have pointed out, propane has the unique property of acting as an anti-solvent for asphalt and heavier oils at temperatures only slightly above atmospheric (80°F. to 210°F.). It may be used, therefore, not only as a precipitant for wax at a low temperature, but also as a precipitant for asphaltic materials at a higher temperature. As shown by Wilson and Keith,[3] the quality of the heavy material precipitated may be varied from high-melting-point asphalt to lubricating fractions by adjustment of the temperature and propane ratio.

Although this paper deals primarily with the combination dewaxing and de-asphalting plant of Shell Petroleum Corporation, it should be pointed out that two other plants have been built and put into operation where de-asphalting is a major function. The 1200-barrel-per-day de-asphalting and acid-treating (in propane solution) plant of the Standard Oil Company (Indiana), at Whiting, Indiana, operates on a high-viscosity Mid-Continent residuum to produce cylinder-stock base by de-asphalting alone, or to produce bright-stock base by de-asphalting and acid treating. The 2000-barrel-per-day-plant to The Texas Company, at Port Arthur, Texas, operates on a variety of stocks, including Mid-Continent residuum and employs propane for de-asphalting only.

GENERAL BASIS OF DESIGN

During the time these developments were being worked out, Shell Petroleum Corporation became interested in the installation of a dewaxing plant at its Wood River refinery; and, as a result of its own research, decided upon the installation of a propane plant. Although the two previous plants had been built to dewax distillates and employed batch-pressure filters for the purpose, it was decided to use continuous filters for the new plant, because they have many advantages over the batch filters, particularly in ease of operation and in obtaining satisfactory drying and washing. The ability to watch the filter operating and make minor adjustments to ob-

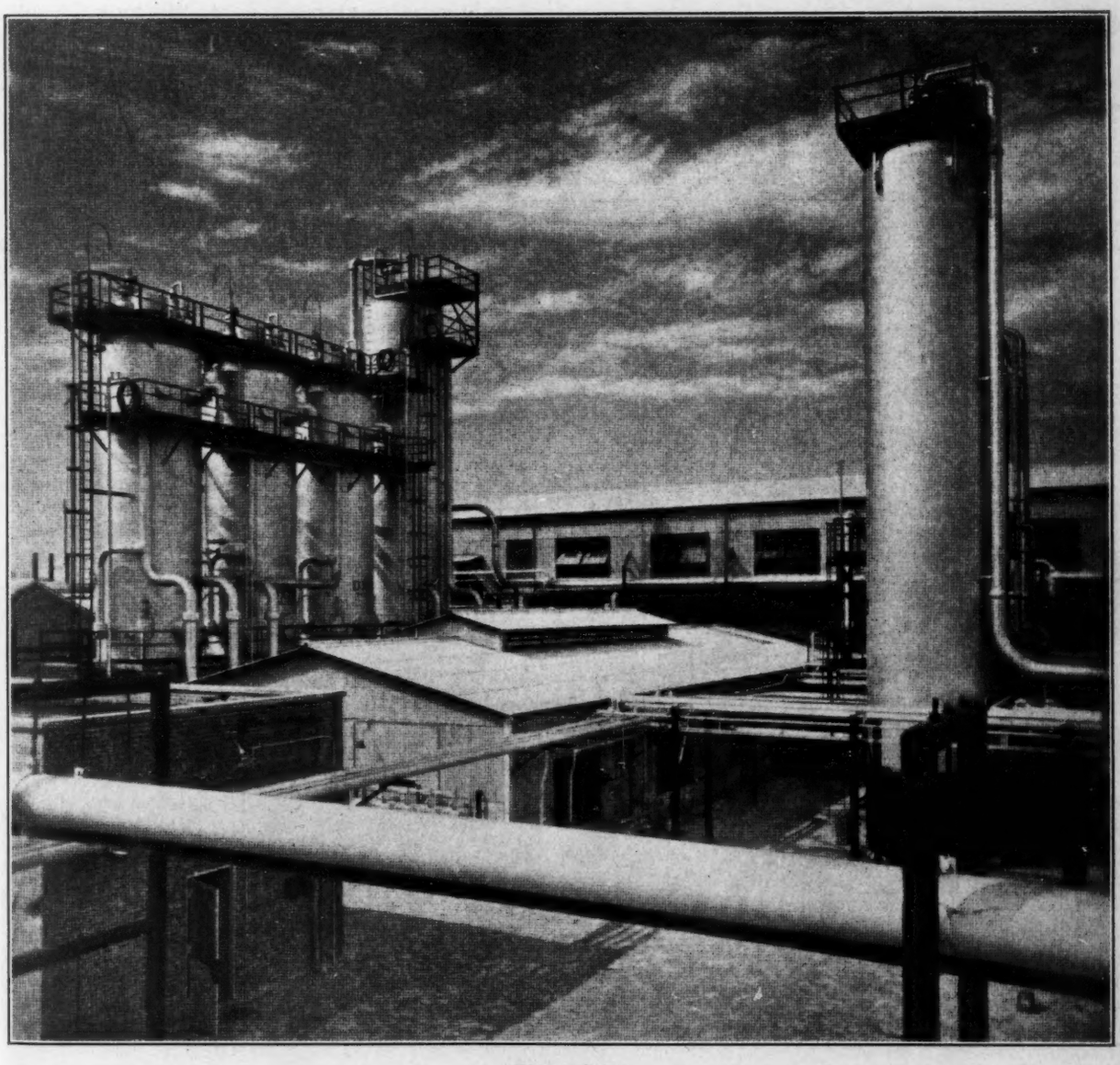


FIGURE 2
Chillers, Pump House, and Filter Building

tain maximum capacity and maximum yield is especially useful. Of course, there were problems to overcome, but all concerned agreed that these could be surmounted. The two problems considered of major importance were: removal of wax from the filter shell, and the prevention of temperature rise from condensing propane in the shell. The latter has never caused any difficulty, and the solution of the former was found to be quite simple—although considerable time was spent in solving it, as discussed hereinafter.

The plant was designed to have a capacity of 2450 barrels per day of dewaxed oil, of sufficiently low pour test so that after subsequent solvent treating and distillation the pour and cloud tests would be satisfactory. These specifications are a very severe test for any dewaxing process; but preliminary experimental work had shown that all cuts would have pour tests of 0°F. or below, and that the cloud would be satisfactory. The charging stock was a long residuum corresponding to about 30 percent of Mid-Continent crude. Approximately 3.5 percent of 170 to 200°F. melting-point asphalt could be removed by precipitation with propane; and the plant was, therefore, designed to include a deasphalting operation.

DESCRIPTION OF PROCESS

A detailed flow sheet of this plant is presented in Figure 1, including minor changes made since the plant originally was put into operation. The process consists of mixing the raw residuum with about 4 volumes of propane, allowing the asphalt to settle, and then removing about 2½ volumes of propane from the upper oil layer. The remaining solution is then chilled to —40°F. by self-evaporation—adding cold propane from the exchange system to maintain concentration, and then filtered to remove wax—and all products are subsequently de-propanized.

In more detail, the flow of materials through the plant is as follows:

Propane from the storage tank **A** is mixed with the residuum charge **B** in the ratio of four volumes to one; and the solution enters the asphalt settlers **C** where the asphalt, containing about one volume of propane, settles continuously by gravity. This fluid-asphalt solution may then be washed in the vessel **W** with a portion of the fresh propane, or the washer may be by-passed and the asphalt solution fed directly to the de-propanizing still **M**.

The de-asphalted solution from the top of the asphalt settler flows through an exhaust-steam pre-heater to the flash chamber **D**, where sufficient propane is removed to reduce the propane to a ratio between 1.5 to 1 and to to 1 by volume. It then enters the warm-solution tank **E**, after having been water-cooled to 100°F.; and this tank supplies surge capacity between the deasphalting and dewaxing systems. From this tank the solution is pumped alternately to each of the 3 chillers **F**, and is there chilled by self-evaporation to —40°F.—the propane being compressed by the compressors **O** and returned through the condensers to the storage tank. Cold propane from the tank **H** is added to the chiller to replace the propane vaporized, and to bring the

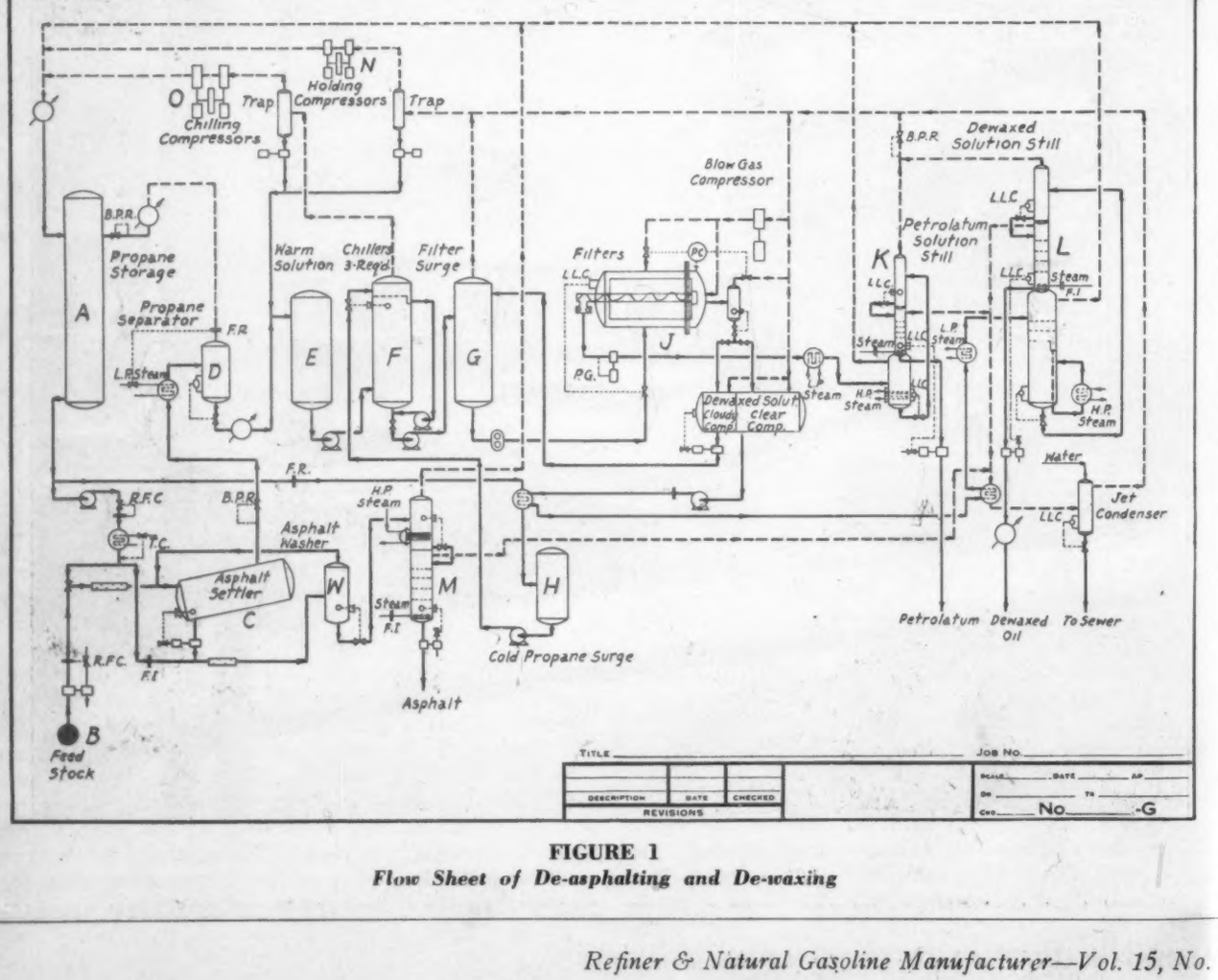


FIGURE 1

Flow Sheet of De-asphalting and De-waxing

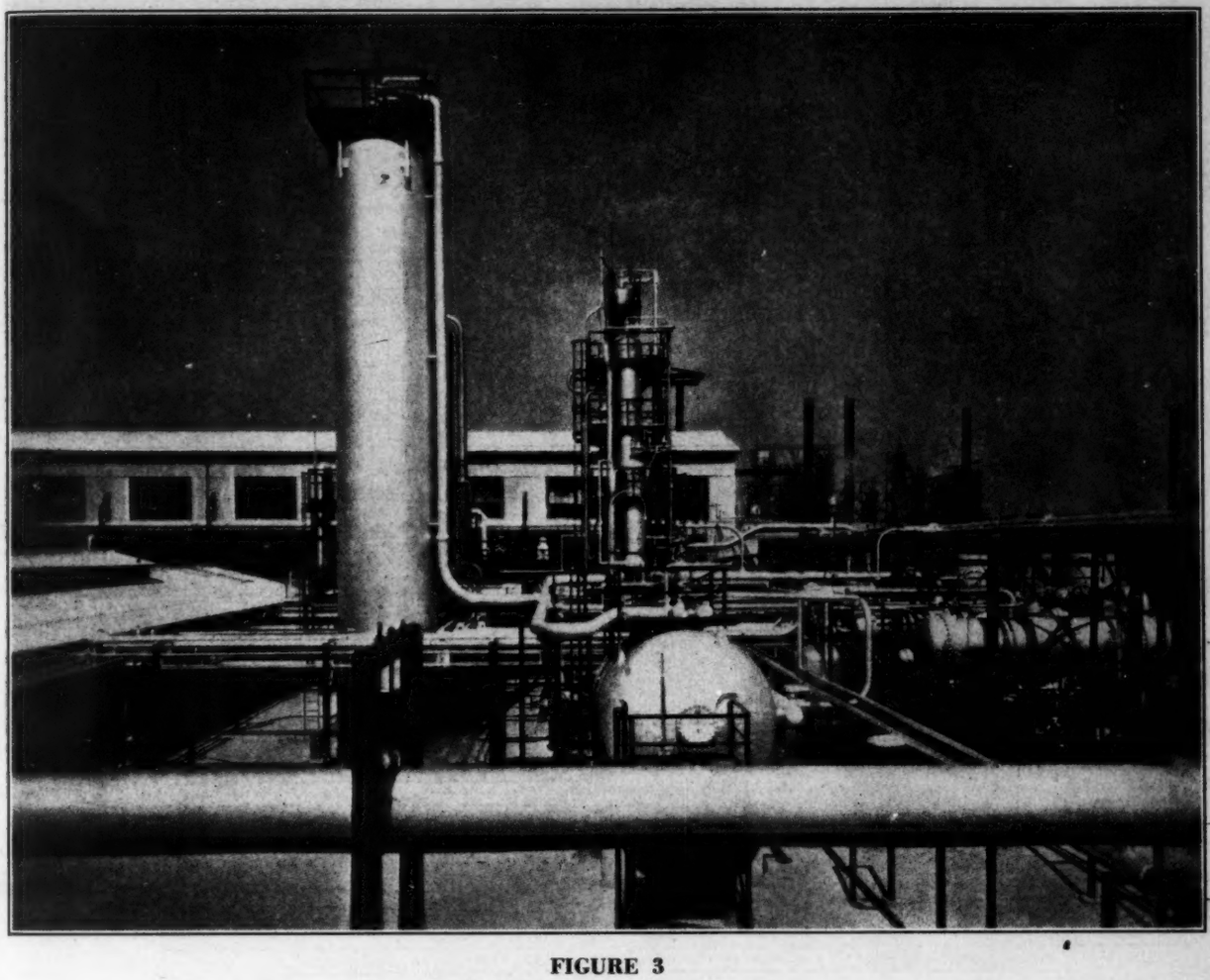


FIGURE 3
Exchangers and Recovery System

chilled solution ratio to 2 to 1. This cold propane is obtained by continuous exchange in a tubular unit against dewaxed solution which is preheated to about 70°F. The chilled solution is then transferred to the filter surge tank **G**, from which it is continuously pumped to the filters **J**.

Dewaxed solution is exchanged against the cold propane flowing to tank **H**, and is then pre-heated by the stripping steam and by exhaust steam before entering the still **L**. Here about 95 percent of the propane is removed at high pressure, and goes directly to the condensers, while the remainder is flashed at atmospheric pressure and then stripped with steam. The wax solution is pumped through an exhaust steam pre-heater to a similar type of still **K**.

DESCRIPTION OF PLANT

A general view of the plant is shown in Figures 2 and 3. In both of these the tall tank in the foreground is the propane storage tank, and Figure 2 shows the switch house and pump house to the left of the propane storage with the 3 chillers and filter-surge tank at the extreme left. The compressor and filter building is in the rear. In figure 3 the asphalt settler is in the center foreground, with the recovery system immediately behind it, and the exchanger and condenser tanks at the right. The warm-solution and cold-propane tanks are directly behind the propane storage tank.

The major parts of the plant, with the exception of the de-asphalting system and the filters themselves, are quite similar to the batch plants previously described; and it does not seem necessary to describe them in any detail. The de-asphalting system consists essentially of a mixing chamber and a settling tank, and the latter is merely a 10-foot by 20-foot horizontal tank with vertical baffles on 3-inch centers, having cross-flow through a manifold running the length of the tank. No difficulties have been experienced with the operation of this system, provided the still temperature is sufficiently high (300°F.) to reduce viscosity and prevent foaming.

The filters themselves may be considered as the most novel part of this plant. Although the design of this filter has been presented before,[3] it is believed that more detailed discussion is pertinent at this time; and a line diagram showing the essential features of its construction is shown in Figure 4. It consists essentially of a rotating sectionalized drum (Oliver-type) which is partially immersed in the propane-oil slurry. The pressure shell enclosing the drum acts also as the pan to hold the slurry. The drum rotates at a variable speed of 3 minutes to 11 minutes per revolution, and with a pressure differential across the drum of 2 to 10 pounds per square inch, with a normal value of about 4 pounds per square inch. Chilled slurry is fed into the shell, under control of a float in the filter to maintain a pre-determined level of 30 to 50 percent submergence.

Figure 5 shows the general features of the filter assembly, with the connection to the master valve at the

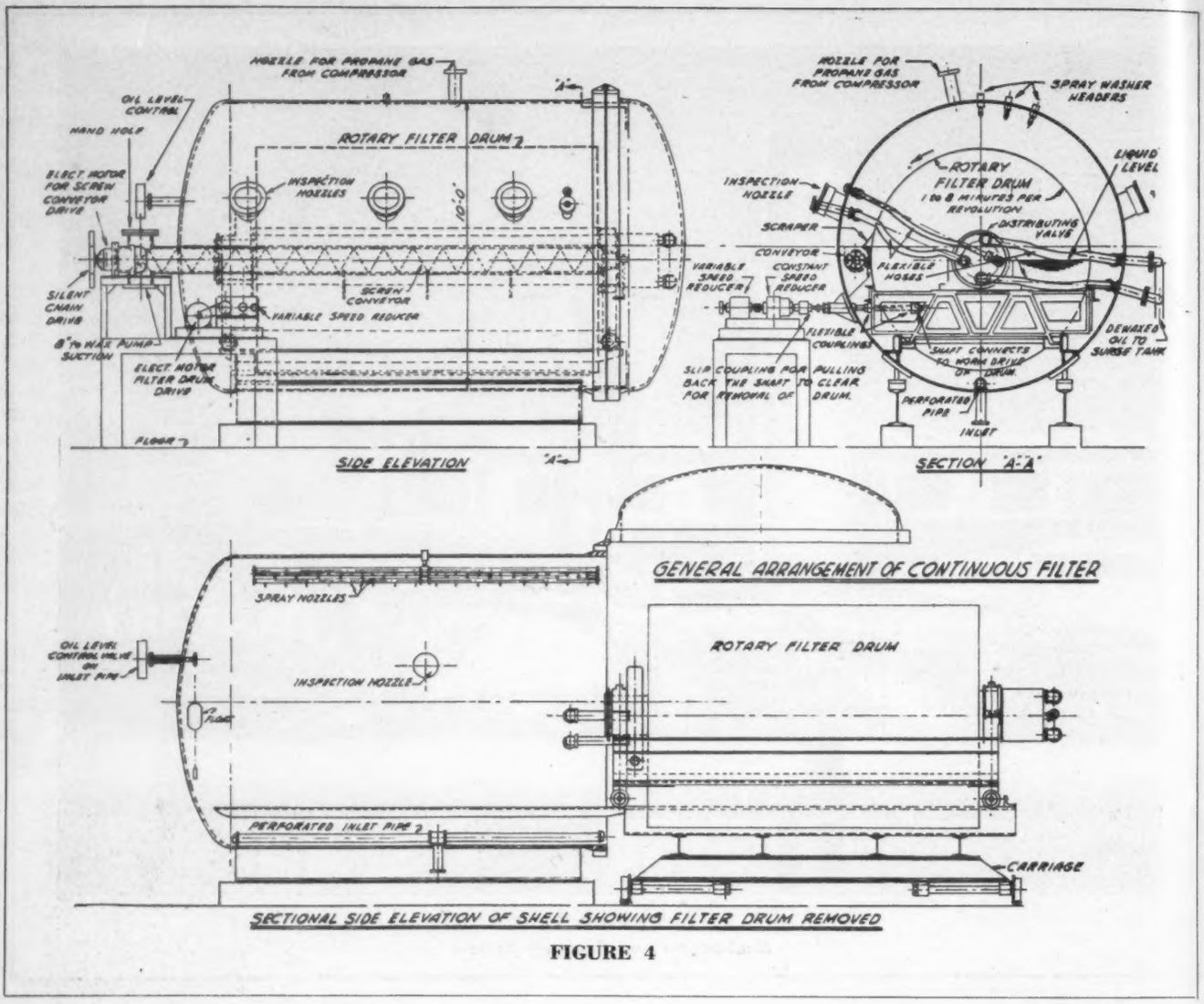


FIGURE 4

open end of one filter. The method of lifting the head and the carriage for receiving the drum when removed from the shell is also evident. Three observation ports just above the conveyor permit usual inspection of the operations at any time. The complete installation of 6 filters may be noted in this photograph. A rear view of the filter, showing various control instruments and the gas separator on the filtrate line, is presented in Figure 6. It may be noted that the solution recovered on the drying operation is included with the normal filtrate, because there is no increase in pour test in the material so recovered.

In the operation of the filter, the drum is rotated below the surface of the slurry, and the super-imposed pressure forms a wax cake due to the fitration of the solution. The drum then rotates through the vapor space where the cake is dried, and finally reaches the scraper where blow-back gas forces the cake from the cloth and onto the scraper blade. It then drops onto a screw conveyor, and passes to the suction of a gear pump. Spray nozzles for washing the cake with propane, or for washing the cloth with hot naphtha, are also shown in Figure 4, as well as the equipment for removing the drum for recovering or for any other purpose.

Particularly impressive is the fact that, from the first batch ever fed to the filters, no serious difficulty has been found with their operation up to the point of removal of cake from the pump. Cakes of about ¼-inch are normal; and the formation, drying and discharging from the drum are very simple operations. At infrequent intervals it is advisable to operate with the dry port partly closed, or with propane in the blow-back in order to improve operation. Such a procedure rapidly clears up any plugging which may occur, and resort to hot kerosene washing is seldom required. Wet blow-back may be used every few days, and hot washing may be required once a month. Even this is a simple procedure, and does not require heating the entire filter.

WAX REMOVAL

Although the very first batch showed that temperature rise in the bowl was of little consequence, and that the filter would operate satisfactorily, it also demonstrated that the wax-removal problem was a serious one. Essentially, this was due to the dryness of the wax cake, which laboratory investigation showed contained much less oil and solvent than had been anticipated from batch-filter and experimental-filter operation. It was impossible to operate for more than an hour, and sometimes less, before the wax pumps would become useless. A number of different types of pumps were tried, some with more or less success, but none was satisfactory.

Laboratory investigations did show that the addition of enough propane to bring the ratio to 1½ to 1 on the wax cake would give a fluid slurry; and, since the wax-

recovery system was designed on the basis of a larger amount of wax cake and a high propane ratio, it was adequate to handle this quantity. The slurry so formed was too low in viscosity for proper operation of the gear pumps, and a secondary piston-type booster pump was, therefore, installed in the line to the wax still, and was controlled to maintain a constant discharge pressure on the gear pumps of about 20 pounds per square inch.

In making this change, propane was fed to the conveyor trough; and the conveyor flights were cut so that it became a mixing device as well as a conveyor. This method of operation was started in the latter part of November, and since that time the plant has been operating continuously with no further difficulties of any kind in the operation of the filters. Filter rates as high as 3.5 gallons to 4.0 gallons of dewaxed oil per square foot (based on total filter area) have been maintained for several days.

CHILLING

During the period from the latter part of November to April 1, the plant was operated at 60 to 70 percent of capacity because of foaming difficulties in the chillers. Although the vapor velocities were thought to be adequately low at the time of design, it was later found that even lower velocities were required to prevent foaming. To correct this condition, it was necessary to install an additional trap and make slight adjustments in the chilling cycle. Since all low-temperature equipment (below 0°F.) is of nickel steel, there was some delay in obtaining material to make this change. It was made during the week of April 6, and the plant has now been operated at full capacity.

OPERATING RESULTS

The plant has been operating for a period of about 6 months, and during most of that time the capacity was approximately 60 percent of design until the changes in the chilling system were made last month. Since that time it has been brought up to full capacity, although insufficient time has elapsed to present operating data at capacity. Only minor changes in operating conditions have been necessary in obtaining the design capacity, so that the general results of the 6 months of lower-rate operation can be considered typical of present conditions. The propane ratios and the temperatures throughout the system are close to those for which the plant was designed, and all units of the plant are now operating as expected. No definite figure is available as to the operating cost; but, in view of the close approach to design conditions, it is believed that it will approximate the figure anticipated.

QUALITY

The pour point of the dewaxed oil has been —10°F. from the start of operation, and there has been no difficulty in this respect — except in those rare instances where leaks were found in the piping and welds of the filter drum itself. Typical inspections of the charging stocks and products from the plant are presented in Table 1.

The most important item in the quality of the oil from

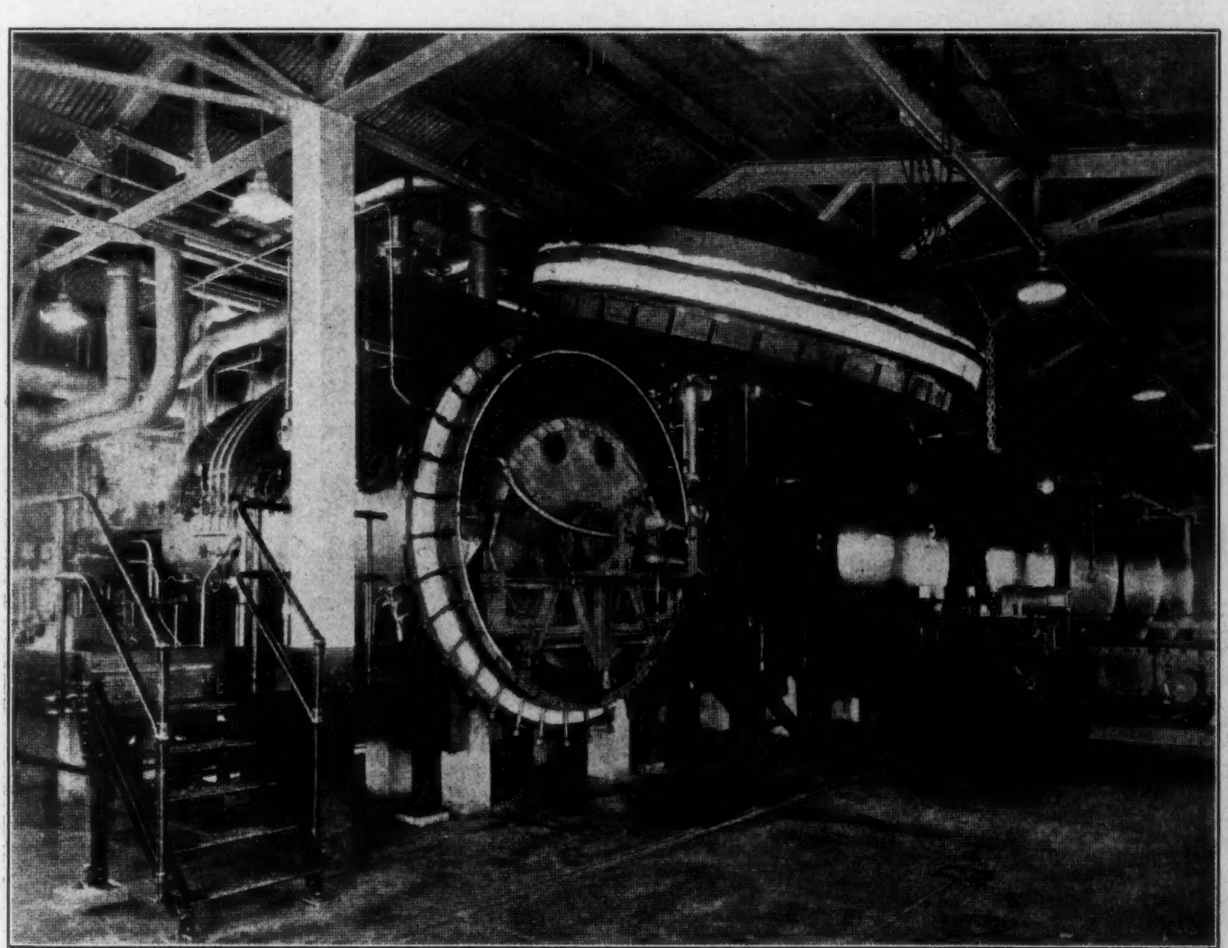


FIGURE 5
View of Filter Assembly

TABLE 1

Inspections of Charge and Products

	Charge	De-asphalted Oil	Dewaxed Oil	Wax	Asphalt
Gravity, deg. A. P. I.	22.5	23.2	22.0	....	....
Gravity, specific	....	....	....	0.918	1.06
Pour point, ASTM	75	80	—10	....	....
Color, Tag-Robinson	....	5 D.D.*	8 D.D.*	....	....
Viscosity, Saybolt Universal, at 130 °F.	598	493	642	....	....
Viscosity, Saybolt Universal, at 210 °F.	106	94	105	72	....
Flash point, °F.	440	440	440	....	....
Melting point, °F.	....	....	....	137	....
Penetration (ASTM) at 77 °F.	....	....	....	....	8
Softening point (ASTM) °F.	....	....	....	....	170

*Double-dilute; diluted 85 : 15 with water-white naphtha, and then diluted again in same manner.

a dewaxing plant is obviously the pour point; and during the entire operating period of this plant, there has been only one 8-hour composite sample which was reported higher than —10°F. pour point, and that was —5°F. Even this, however, is not the only criterion of the thoroughness of the dewaxing operation. The oil in this plant is subsequently solvent-extracted to about 100 viscosity index, with a rise in pour point of about 5°F. under normal conditions and 10°F. under the most adverse conditions. The treated long residuum is then distilled to produce several cuts, the lightest having a viscosity of 110, Saybolt Universal, at 100°F., and the pour test of all cuts is normally 0 or —5°F. At infrequent intervals the lightest cut may show a pour test of + 5°. Of even greater significance than this is the fact that all cuts show no tendency to cloud when held at 20°F. indefinitely.

The color of the dewaxed oil is also deserving of some attention. The dark residuum is de-asphalted to remove about 3.5 percent of 170-melting-point asphalt, and then has a color of 5 D.D. Tag-Robinson. After dewaxing, the color has improved to 8 D.D., and the color is noticeably improved over that of the de-asphalted oil and the cast is very good. The concentration of color bodies in the wax may be noted from its very dark color.

(*Continued on page 218*)

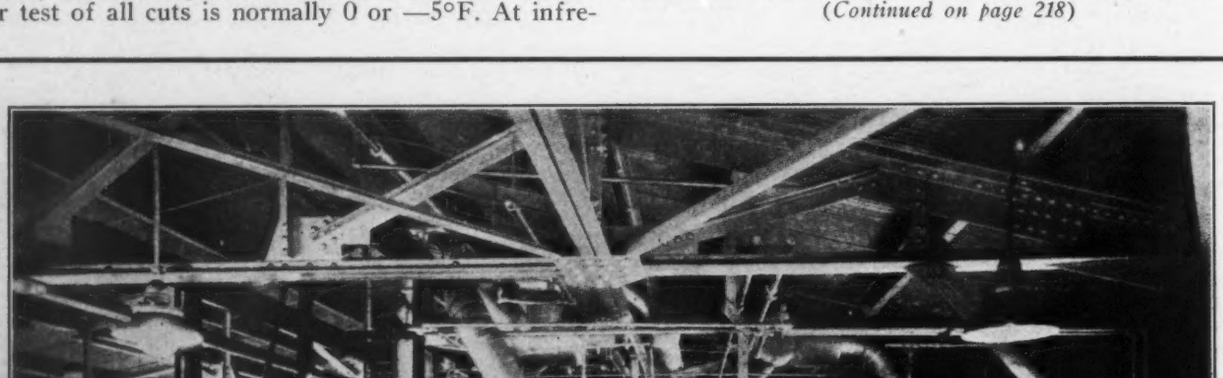


FIGURE 6
Rear View of Filter

Color Restoration of Gasoline and Kerosene in the Field

J. B. RATHER and L. C. BEARD, JR.
Socony-Vacuum Oil Company, Inc., New York

Before Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 14, 1936.

THE discoloration of gasoline and kerosene initially refined to a water-white color, when held for some time in storage, has for many years been an annoying and, in many instances, a costly problem to the petroleum industry. The problem has, perhaps, been more acute in the case of export gasoline and kerosene than in domestic markets. This, of course, is largely due to the longer storage periods entailed in export distribution and also to the difficulties involved in shipping discolored products back to the refineries for reconditioning. In domestic markets gasoline, several years ago, gave rise to the greatest amount of trouble; but the introduction of colored gasolines has, to some extent, ameliorated this situation. With kerosene, however, the trade is becoming more critical in demanding a colorless product. In a measure, this is due to the introduction of range burners equipped with glass containers holding several gallons of kerosene, which make any discoloration more evident to the purchaser.

To give some idea of the magnitude of the losses which might be sustained when kerosene goes off color in bulk storage, the following example is of interest. In India in 1928 there were generally marketed two grades of burning oil—one of which was white in color, and had satisfactory burning characteristics; the other was yellow in color, and a relatively low-grade product of poor burning characteristics. The price differential between these two grades was approximately one rupee (37 cents) per 10 gallons. Whenever any oil initially white and of good burning characteristics went off color, it was assumed by the trade that it was the inferior burning product, and a reduction in price of approximately one rupee per 10-gallon unit was insisted upon. In the case of an 80,000-barrel tanker this would entail a loss in the neighborhood of $140,000 if it became necessary to dispose of the discolored oil at this price reduction.

We have been investigating this problem for more than 10 years. It was early found that the discoloration of kerosene and gasoline during storage was due to oxidation, and that samples of kerosene stored in an inert atmosphere in the absence of oxygen maintained their initially colorless condition for a long period of time; whereas those stored in air went off color much more quickly. Our initial efforts were directed toward the development of oxidation inhibitors which would act as color stabilizers. A number of compounds were found which, added to kerosene and gasoline in concentrations as low as 1 pound to 15,000 gallons, effectively stabilized the color. Among these compounds were the following: thiocarbanilid,[1] hydroquinone,[2] resorcinol,[2] pyrocatechin,[2] pyrogallol,[3] phloroglucinol,[3] 1,2,4-trihydroxybenzene,[3] butyl pyrogallol,[4] alkyl substituted dihydroxybenzene,[5] alkyl substituted polyhydroxybenzene,[6] ethanolamines,[7] urea,[8] and thiourea.[8] Many of these compounds are also effective inhibitors of the formation of gum in gasoline—which, of course, is also an oxidation phenomenon. Some idea of the effectiveness of these inhibitors in preserving the color of refined kerosene can be gained from the following tabulation, which is based on the examination of more than 100 cases of oil, half of which were stabilized with pyrogallol in a proportion of 1 pound to 10,000 gallons, and half of which were unstabilized. These cases were shipped abroad and stored in tropical warehouses for six months, and then shipped back to this country for examination. The initial color of the oil was somewhere between 18 and 21.

Number of cases examined.....111
Age of samples when examined.....10 to 14 months
Stabilizer (pyrogallol).....1 lb. per 10,000 gal.

Percent of cans which were:

	Stabilized (Percent)	Unstabilized (Percent)
+12 and higher	81.62	14.30
0 to +12	17.44	44.20
−1 and lower	0.94	41.50

In the course of our investigation leading to the development of these color stabilizers, it was found that certain of these compounds, in particular the polyhydroxybenzenes such as hydroquinone, pyrogallol, and diamyl hydroquinone, possessed the property of decolorizing kerosene and gasoline which had gone off color in storage. In many cases, the color was restored to very nearly the initial color of the oil when freshly refined, and the restored color was retained by the oil without subsequent discoloration for periods as long as six months. The preferred procedure of effecting this decolorization is to dissolve 1 pound of, for example, hydroquinone in 1 gallon of a suitable solvent, such as *iso*propyl or ethyl alcohol, and treat the oil under good agitation with this solution in the proportion of 1 gallon of solution to from 2000 gallons to 15,000 gallons of oil, depending upon the degree of discoloration and the age of the oil. After decolorization has been effected, it is preferred to store the oil in the absence of water; since oil decolorized with this reagent will revert to its colored

[1] U. S. Patent No. 1,916,438.
[2] U. S. Patent No. 1,951,205 and 1,951,208.
[3] U. S. Patent No. 1,951,206 and 1,951,207.
[4] U. S. Patent No. 1,959,315.
[5] U. S. Patent No. 1,959,316.
[6] U. S. Patent No. 1,959,317.
[7] U. S. Patent No. 1,989,528.
[8] U. S. Patent No. 2,002,645.

condition if intimately mixed with water to such an extent that the decolorizing agent is removed because of its greater solubility in water. It is believed that, since vigorous shaking with water will cause the color to return to the oil, the mechanism of the decolorization phenomenon is due to the formation of some loose addition compound.

In some cases it may be found that decolorization with these materials does not raise the oil to marketable color. In these instances, if the oil has been raised to a color of +14 or higher, additional treatment can be made with an oil-soluble neutralizing material which in concentrated solutions gives a blue to a violet color. In the concentrations in which these materials are used practically, however, the amount of blue-violet neutralizing material added is just sufficient to counteract any residual color not removed by the first treatment. These oil-soluble blue-violet neutralizing materials can also, of course, be used on oil directly without preliminary treatment, provided the color of such oil is not lower than +14. The cost for decolorization of oil by treatment with hydroquinone and the blue-violet neutralizing material will be somewhere in the neighborhood of 1 cent per barrel. This process has been used commercially for a period of 8 years, with very material savings. In 1928 it was first utilized in India, China, Indo-China, Straits Settlements, and Netherlands East Indies under the most adverse climatic conditions with entire success, and from that time until this has been used successfully both here and abroad, with savings that mount into seven figures.

One point of interest, in this connection, is that in the case of any one oil produced from any one crude, and by the same method of refining, only a certain proportion of this oil will go off color—depending largely upon the conditions of storage and catalytic contaminants which might be present. It is obviously uneconomical to refine all oil to the extent necessary to insure that no small part of it under unusual and severe conditions of storage will go off color. Considerable savings in refining expense can, therefore, be realized by refining only to such an extent as is necessary to afford reasonable color stability, and then decolorize in the field such oil as may go off color.

Propane De-Asphalting and De-Waxing

(*Continued from page 216*)

YIELDS

Average-yield figures over long periods of time show 78.0 percent dewaxed oil, 18.5 percent wax, and 3.5 percent asphalt. Based on de-asphalted oil, the dewaxing yield has been maintained at 81 percent. For some consecutive days, yields as high as 85 percent have been obtained, and it is anticipated that a yield of 83 percent will be normal after the next few weeks of operation.

The wax produced has a melting point of 137°F.; and frequently shows an oil content, determined analytically, of less than 30 percent. Although the plant was not designed for washing, some preliminary experiments have been made with sprays in the filter, which indicate that the oil content may be reduced easily to about 15 to 20 percent by this simple method. As indicated above, some small amount of dark-colored semi-asphaltic bodies is removed in the dewaxing operation, so that it would be expected that the actual yield might be slightly lower than that calculated from the wax contents of the charge stock and the final wax cake. The actual yield over a long period of 81 percent is 4 percent higher than that used as a basis for design of the plant.

CONCLUSIONS

The foregoing discussion has shown that a propane dewaxing plant has been in operation for about 6 months and has demonstrated two very important points: 1, that commercial continuous filtration in propane solution is entirely satisfactory; and, 2, that it is possible, with propane, to dewax a Mid-Continent long residuum so thoroughly that the dewaxed oil may be solvent-treated and distilled to produce oils of satisfactory pour and cloud test.

Although the authors have been given the privilege of presenting the information on the operation of this plant, it should be pointed out that the solution of the two major problems was due to the cooperative spirit of all concerned with the project. Especially is acknowledgment due to the entire operating personnel of the Shell Petroleum Company lubricating-oil department, and to J. T. Dickinson of The M. W. Kellogg Company, who was largely responsible for working out problems connected with filter operations, as well as other problems involved in the plant as a whole.

BIBLIOGRAPHY

[1] W. H. Bahlke, R. N. Giles, and C. E. Adams, "Dewaxing Oils in Propane Solution with Self-refrigeration," *Proc. A. P. I.* **14M** (III) 16 (1933).

[2] U. B. Bray, C. E. Swift, and D. Carr, "Use of Propane in Lubricating-Oil Refining," *Refiner and Natural Gasoline Manufacturer*, p. 333, Sept. 1934.

[3] R. E. Wilson and P. C. Keith, Jr., "Recent Developments in Propane Technique," *Proc. A. P. I.* **15** (III) 106 (1934).

Clay Treating of Motor Fuels

M. R. MANDELBAUM
The Gray Processes Corporation, Newark, N. J.
and
PAUL F. SWANSON
The Kellogg Company, New York, N. Y.

THE Gray, the Osterstrom, and the R. K. Stratford clay-treating processes are in use to the extent of more than 180,000 barrels per day throughout the world. Of this, some 140,000 barrels (operating and under construction) is in the United States.

Correlation of available data on the Gray process, which is the most widely used, is made difficult by differences in the oil treated, specifications to be met, and design limitations. This is reflected in clay life ranging from 800 barrels to 27,000 barrels per ton of fullers earth.

Data have recently become available on two high-pressure Gray process installations, one of which operates at a high, and the other at a low throughput rate (approximately 5 barrels and 1 barrel per ton per hour, respectively.) The first plant, in connection with a 30,000-barrels-per-day combination cracking unit operating on East Texas crude, has four Gray towers in parallel, and has attained a clay life of more than 27,000 barrels per ton. This plant supplements clay treating with b.a.p. inhibitor, and reports that the inhibitor susceptibility of the clay-treated gasoline is almost double that of the unclayed cracked product.

The other plant uses two Gray towers in series, and at a clay life of more than 4,000 barrels per ton produces a cracked gasoline that is remarkably stable as to color and copper-dish gum.

Other recent developments include the Gray treatment of cracked gasoline from topped Kettleman Hills crude, and installations in connection with units producing polymer gasoline. In the latter instance, clay life of 20,000 barrels per ton has been obtained.

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 14, 1936.

THE first commercial installation for the clay treating of motor fuel was made 12 years ago, in 1924. It represented a jump from a pilot-plant installation, charging a few pounds of fullers earth, to an 8-ton tower. It was predicted that 2,000 barrels of cracked gasoline could be treated before it would be necessary to re-charge the treating vessel. This would have been equivalent to a throughput of 250 barrels per ton of earth[1]. The intervening years of development are, in a sense, summed up by a run recently completed in a unit of four clay towers, with a charge of more than 100 tons of fullers earth, during which the throughput exceeded 27,000 barrels of cracked gasoline per ton of clay.

There is no need to repeat here a detailed discussion of the theory of clay treating. As is well known T. T. Gray[2] made the fundamental discovery that vapor-phase treatment of cracked gasoline with adsorbents of the clay type resulted in the polymerization of the objectionable unsaturated hydrocarbons, and that in this way a selective treatment could be achieved which would obviate the disadvantages of the then commonly-used refining agent—sulfuric acid.

Gray preferred to pass the vapors being treated through the adsorbent, and the commercial development of the Gray process continued in this direction[3]. Later, R. K. Stratford[4] found that the specific problem confronting him could best be solved by countercurrent treatment of cracked-gasoline vapors with a slurry of fine clay in naphtha; and Osterstrom achieved certain advantages for still another type of problem by subjecting the cracked gasoline to treatment under high pressure, thereby maintaining it in liquid phase at polymerizing temperatures. All three processes are in commercial use, but the latter two have until recently been limited in their application to the refineries of the companies in which they originated; while the Gray process, simpler and of more general adaptability, has received wider use. The magnitude of this is shown in Table 1 which gives, in round numbers, the commercial use (operating and under construction) of the three methods.

TABLE 1

Clay Treatment of Motor Fuel
(Operating and Under Construction)

	United States	Other Countries	Total
	(Barrels per Day)		
Gray process	125,000	15,000	140,000
Osterstrom process	16,000	500	16,500
Stratford process	.....	30,000	30,000
Total	141,000	45,500	186,500

This acceptance of clay treating has been encouraged by recognition of its advantages and economics: a refined cracked gasoline is obtained, improved as to color, gum, and stability; operating costs and losses are lower than those of other processes which achieve the same results; and there is no loss in octane number due to the treatment.

Descriptions and general flow diagrams of the three processes discussed, as well as summaries of the results obtained, have been published. The sections on the Osterstrom and R. K. Stratford processes, in the Cooke and Hayford paper,[5] are quite complete; and additional data on the former have been included in a recent paper by Morrell and Egloff.[6] One of the present authors, in a paper before the World Petroleum Congress[7] of 1933, gave considerable data on several applications of the Gray process as used to refine gasolines produced by cracking from various charging stocks under different treating conditions. Since that time developments of interest include additional data on the Gray process at ele-

vated operating pressures. This paper is largely concerned with a presentation of this newly-available data.

Attempts to correlate the available data on the commercial practice of clay treating result in the conclusion that exact analysis or rigid treatment which would permit of generalized conclusions is not applicable, and that each example is a case by itself insofar as quantitative deductions are concerned. This is indicated, at first glance, by the fact that plants in commercial operation have reported clay life ranging from 800 barrels to 27,000 barrels per ton of earth. This divergence is due to a number of variables which we have designated, for convenience, as factors of "treatability," which involve the ease or difficulty of handling the individual product; "specifications," which include the requirements of each individual refiner; and "design," or allowable modifications in clay-treating equipment which will give the maximum permissible economy of installation and operation for any particular problem. These factors, which have been discussed in previous papers already referred to, can be summarized as follows:

TREATABILITY FACTORS

a. Base of crude: Ease of handling cracked gasoline increases with paraffinicity of cracking stock.

b. Cracking charge: Gasolines from distillate stocks are easier to treat than those from residuals.

c. Cracking conditions: The more severe these are, the greater the treating difficulty. Usually, drastic cracking conditions are indicated by high transfer-line temperatures and production of relatively high percentage of gas.

d. Sulfur content in charge: This does not affect activity of clay as regards color improvement, gum reduction, etc.; but clay treatment under usual conditions of commercial application brings about little or no reduction in the sulfur content of the vapors treated.

SPECIFICATION FACTORS

a. End point of cracked gasoline: This in turn affects color, gum, and induction period; but not in the same direction.

b. Initial color: Most clay-treating operations use this property for control even when the resultant gasoline is to be dyed. Specification varies from 17 to 30.

c. Color-stability tests:

1. Sunlight exposure is frequently used to test both sour and sweetened samples. Specification varies.

2. Color hold on dark storage is sometimes tested by direct or accelerated methods.

d. Copper-dish gum: This is the test most frequently used for control specification on cracked gasoline, the limiting value ranging from 10 to 40 milligrams.

e. ASTM or other air-jet gums: Tests of this nature are seldom applied for control purposes, and then only for vapor-phase cracked gasolines and others having comparatively high gum content.

f. Induction period: Voorhees and Eisinger[8] method or bomb method sometimes used for control. Specification varies over wide range.

The control tests are performed on the cracked gasoline alone, or on the final blend of cracked and straight-run gasolines. The tests performed and the

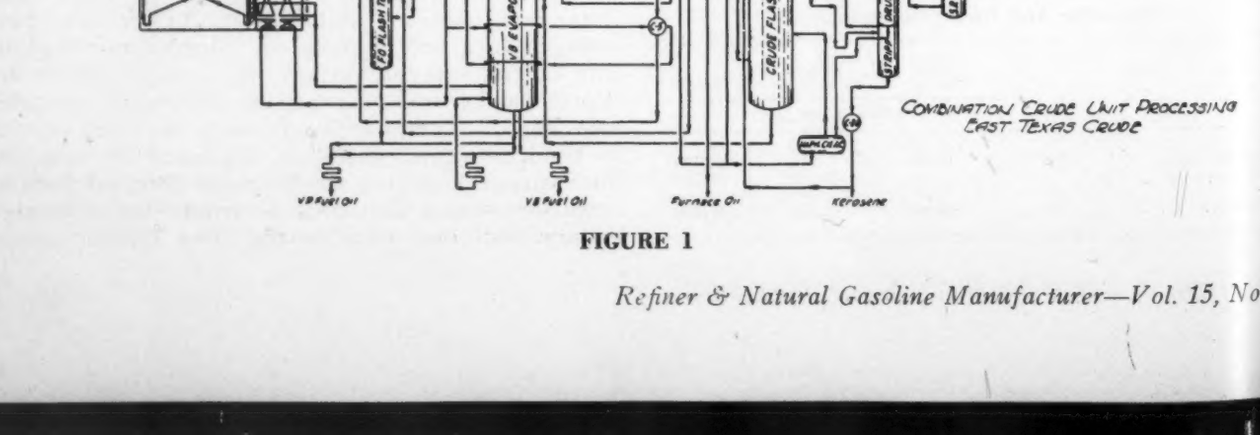


FIGURE 1

criteria applied depend on the marketing practice of the individual refiner, and on whether or not he supplements clay treating with inhibitors.

DESIGN FACTORS

a. Ratio between quantity of gasoline to be treated and amount of clay (barrels per ton per hour).
b. Treating temperature and pressure.
c. Number and arrangement of clay beds.
d. Ratio of depth to diameter of clay beds.
e. Type of adsorbent used.
f. Recirculation or non-recirculation of part of treated gasoline through clay.
g. Difference in end point between raw product entering clay tower and vapors leaving polymer bubble tower.
h. Time of contact (depends on [a] and [b]).
i. Vapor velocity (depends on [a], [b], [d], and [f]).

Large differences in clay-treating temperature and pressure have been found greatly to affect clay life. This has made it possible to obtain the long clay life and efficiency of treatment observed with recently-built cracking units operating on residual stocks at high cracking temperatures (in the neighborhood of 1000° F.).

Steininger[9] emphasized the importance of time of contact, which has an important bearing on clay life. However, this feature alone cannot be said to control results. Laboratory and pilot-plant runs have established the fact that with all other conditions the same, including time of contact, large differences in operating efficiency and economy can be obtained by varying the vapor velocity. Similarly, under some conditions relatively small variations in temperature and pressure are of great importance as measured by results obtained.

TABLE 2
Range of Operating Conditions of Gray Towers

Amount treated per day, bbl.	80 to 12,000
Octane No., ASTM	55 to 80+
Number of Gray towers	1 to 6
Arrangement	Single, parallel, series
Diameter of towers, ft.	5 to 25
Depth of clay bed, ft.	6 to 25
Gasoline per ton of clay per hour, bbl.	0.5 to 6.1
Time of contact, sec.	20 to 400
Treating Temperature, deg. F.	250 to 475
Treating pressure, lb. per sq. in.	5 to 380
Pressure drop, lb. per sq. in.	2 to 50
Throughput per ton of clay, bbl.	800 to 27,000

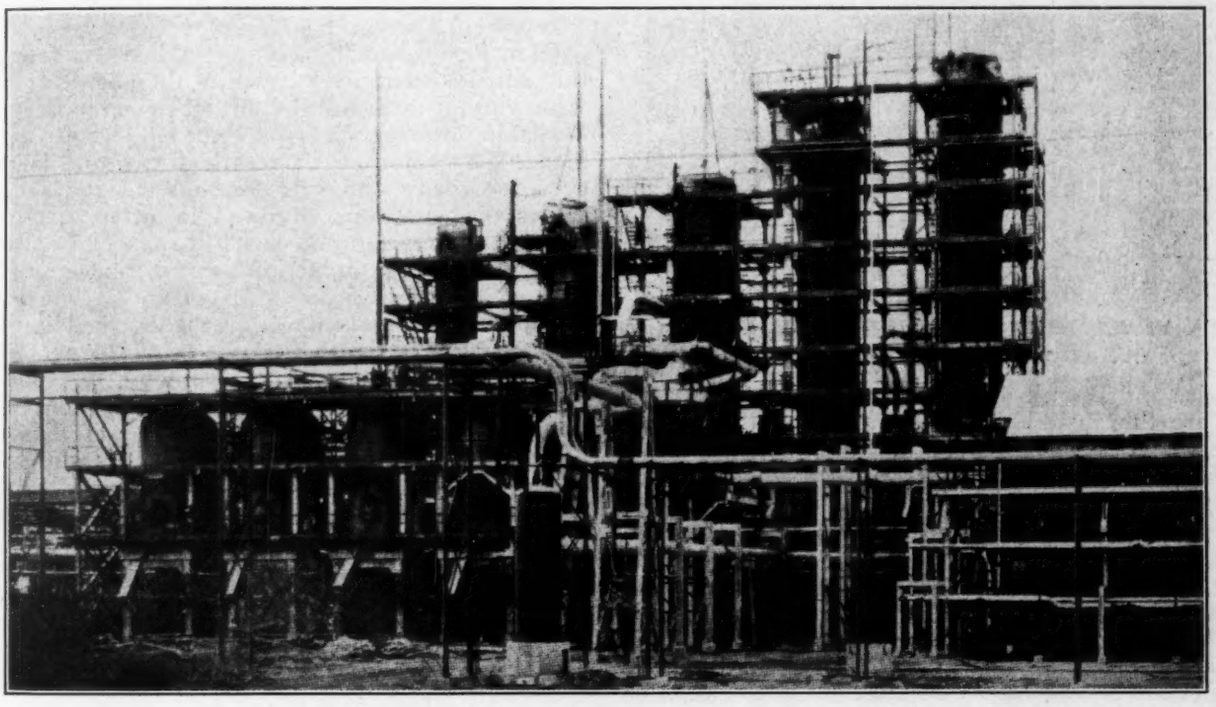


FIGURE 2
Four Clay Towers Connected with 30,000-barrel Day Combination Unit.

We have indicated by the foregoing discussion that the flux of interrelated and independently-varying factors makes it difficult to generalize as to Gray tower performance. Table 2 shows the wide range of commercial results obtained on re-run and direct-connected Gray treatment of cracked gasoline from Cross, Dubbs, Holmes-Manley, Tank and Tube, Gyro, combination, and other cracking units.

The lowest yield per ton of clay indicated was experienced with a highly-cracked gasoline refined to meet rigid specifications. The high yield was obtained in one of the plants described hereinafter. Both are extremes. A normally-cracked product from a representative charging stock should be expected in a properly-designed Gray-tower installation, operating at a pressure of 40 to 60 pounds per square inch, to treat a minimum of 2000 barrels of cracked gasoline per ton of fullers earth to specifications which will enable the product to be marketed unblended, uninhibited, and undyed. Where higher operating pressures (150 to 200 pounds per square inch) are used, a corresponding clay life of 4000 barrels per ton may be expected.

TABLE 3

Average Properties of Gasoline vs. Clay Life

(Gray towers connected to 30,000 Barrel per day combination unit)

Clay Life (Barrels Per Ton)	Cracked Gasoline	Blend of Cracked and Virgin Gasoline to Run-down Tanks				
		Color		Induction Period*		Copper-Dish Gum
	Color	Sour	Sweet	Sour	Sweet	(Sweet)
0- 1,000	30+	30+	30	500	375	2
1,000- 2,000	30	29+	30+	695	385	4
2,000- 3,000	30+	30+	30+	535	375	4
3,000- 4,000	29+	30+	30+	520	270	4
4,000- 5,000	30+	30+	30	430	280	4
5,000- 6,000	30+	30+	30+	295	225	5
6,000- 7,000	30	30+	30+	455	240	6
7,000- 8,000	25+	26	25+	395	345	5
8,000- 9,000	25	27	27	355	290	6
9,000-10,000	24	25	25+	545	345	8
10,000-11,000	25+	26	25+	...	335	17
11,000-12,000	26+	26+	26+	350	285	6
12,000-13,000	28+	28+	28+	405	305	5
13,000-14,000	30	28+	27	...	275	6
14,000-15,000	29+	29+	27+	...	300	6
15,000-16,000	30	30+	30	...	270	6
16,000-17,000	29+	30	29+	...	280	5
17,000-18,000	29	29+	29	...	315	4
18,000-19,000	28+	28+	28+	490	375	5
19,000-20,000	28+	....	....	...	335	..
20,000-21,000	29	....	....	...	275	..
21,000-22,000	28	....	....	...	300	13
22,000-23,000	27	....	....	...	275	14
23,000-24,000	26+	....	....	...	270	22
24,000-25,000	26+	....	....	...	245	13
25,000-26,000	25	....	....	...	275	13
26,000-27,000	25+	....	....	...	300	10

*Voorhees and Eisinger method.

DATA FROM HIGH-PRESSURE GRAY TREATING AT HIGH THROUGHPUT RATE

Price and Brandt described[10] in a general way the clay-treating installation in connection with a 30,000-barrel-per-day combination cracking unit operating on East Texas crude, and presented an extended discussion of the results obtained. Additional runs on this equipment show results that are even better than those given in that paper. A simplified flow diagram of the complete installation (Figure 1) shows the inter-connection between the clay towers and the cracking plant. Figure 2 shows the clay towers as an integral part of the unit. The installation in question is noteworthy because of the combination of high throughput per ton of clay and high treating rate, expressed in barrels per ton per hour. This is accounted for by a combination of circumstances, including high clay-treating pressure and the fact that, although only the cracked product is passed through the clay towers, cracked and straight-run gasoline from the combination unit are ordinarily routed to the same run-down tanks—so that the critical properties are the tests on the blend, rather than on the cracked gasoline alone. Still another cause for the long clay life is the use of an inhibitor to supplement the treating action of the clay. This minimizes induction period as a criterion of clay efficiency, and makes it possible to use the clay for longer cycles than would otherwise be the case.

Table 3 summarizes a recent run which was concluded after a throughput of more than 27,000 barrels per ton, during which treating conditions were substantially those given by Price and Brandt. Since the towers charge 105 tons of clay, this represents a throughput on one charge of clay of 2,800,000 barrels during a period of more than 9 months. For this plant the time of contact, calculated on the basis of the perfect gas laws by Price and Brandt, is 110 seconds. The treating rate is 4.8 barrels per ton per hour when the combination unit operated for ultimate gasoline production.

The data given in this table, and plotted in Figure 3, represent average conditions for each 1000 barrels per ton throughput. Since the cracked gasoline from this unit is ordinarily blended in the run-down tanks with varying amounts of straight-run, most of the available information is on the properties of the blend. The color of the cracked gasoline is, however, recorded as an index of clay activity. Figure 4 shows the variations (during the latter part of the run) in percentage of straight-run, end point of cracked gasoline, induction period, and gum. The extreme fluctuations are caused by the changes in end point and percentage of the cracked gasoline. During parts of this period the straight-run concentration was zero, and corresponding tests on the cracked product can be read from the graphs.

We have already referred to the fact that clay-treated gasoline is especially responsive to inhibitors. Table 4 shows the octane number, inhibitor response, and other tests of cracked gasoline from the same plant before and after clay treating. These samples were re-distilled in order to obtain conformity of distillation range. Note the fact that, even at the high clay life already reached, induction period of the cracked gasoline is more than doubled by clay treating, and the b.a.p. response is also almost doubled.

DATA FROM HIGH PRESSURE GRAY TREATING AT LOW THROUGHPUT RATE

In comparison with the above plant may be taken one running at conditions tending to produce a more highly refined cracked gasoline. This plant has two Gray towers, each 6 feet in diameter with a 28-foot clay bed, and a clay charge of 16 tons for each tower. The towers here are arranged in series, followed by a polymer fractionator, and operating conditions as given in Table 5 obtain.

TABLE 4

Gasoline Improvement Resulting from Clay Treating

Clay life, bbl. per ton	23,600	
Sample	Inlet	Outlet
Gravity, deg. API	56.0	56.3
ASTM Distillation in Deg. F.		
Initial boiling point	106	104
10-percent point	162	158
50-percent point	266	266
90-percent point	344	344
End point	380	379
Octane No., CFR motor method	68.1	68.0
Copper-dish gum, milligrams	103	26
Induction period, min.	145	330
Induction period of sample plus 0.001 percent b.a.p.	335	680
B.a.p. response per 0.001 percent min	190	350

TABLE 5

Operating Conditions

Charge to cracking unit	28-deg. reduced Kentucky crude
Transfer temperature, °F.	965 to 970
Octane No. of cracked gasoline, ASTM	70
Distillate entering, bbl. per day	1365
Distillate returned as reflux, bbl. per day	440
Net make, bbl. per day	925
Operating pressure (inlet), lb. per sq. in.	175
Operating temperature, °F.	430
Bbl. per ton per hour	1.2
Time of contact, sec.	258

Note that in this case reflux material for the main bubble tower is obtained from the gasoline receiver. As pointed out by Steininger, this does not change

TABLE 6

Data from Unit Operating as in Table 5

Total Throughput (Barrels Per Ton of Clay	Dark Storage Colors (Saybolt)				"Sun Color"	GUM—Dark Storage (Copper-Dish)				No. Times Clay Steamed	Throughput Since Steaming (Barrels)
	Initial	30 Days	60 Days	90 Days		Initial	30 Days	60 Days	90 Days		
186	+30	+30	+30	+30	22	1.2	6.0	9.2	3.5	0	...
292	+30	+30	+30	+30	21	7.4	10.9	2.8	13.1	0	...
362	+30	+30	+30	+30	11	3.0	1.7	0.0	1.3	0	...
458	+30	+30	+30	+30	26	0.1	0.2	1.2	1.1	1	85
606	+30	+30	+30	+30	23	1.1	4.1	2.5	7.2	1	232
825	+30	+30	+30	+30	22	2.3	0.8	1.1	0.6	1	451
983	+30	+30	+30	+30	23	0.7	1.7	6.1	2.7	1	610
1,082	+30	+30	+30	+30	18	2.7	6.1	6.6	7.1	2	90
1,228	+30	+30	+30	+30	18	10.9	18.9	7.9	4.5	2	235
1,256	+30	+30	+30	+30	16	3.2	4.9	4.7	5.5	2	264
1,477	+30	+30	+30	+30	25	3.6	3.2	2.0	1.5	3	184
1,629	+30	+30	+30	+30	23	4.6	7.7	0.2	0.7	3	236
1,857	+30	+30	+30	+30	22	24.3	12.1	2.2	2.2	3	464
1,962	+30	+30	+30	+30	18	3.2	0.3	7.2	0.4	4	51
2,100	+30	+30	+30	+30	22	9.8	9.2	4.7	1.3	4	188
2,285	+30	+30	+30	+30	25	11.9	11.9	8.8	10.1	4	373
2,415	+30	+29	+30	+30	22	16.5	14.5	1.4	5.1	4	503
2,609	+30	+30	+30	+30	25	4.1	1.2	2.6	4.0	4	697
2,773	+30	+29	+29	+29	25	5.5	12.5	8.8	5.3	4	889
2,958	+30	+30	+30	+30	25	1.5	3.5	2.8	3.0	5	185
3,300	+30	+30	+30	+30	25	4.2	3.1	2.7	10.1	5	527
3,517	+30	+30	+30	+30	15	9.8	10.6	10.4	10.6	5	840
3,794	+30	+30	+30	+30	22	1.6	1.2	5.1	1.0	6	121
3,918	+30	+30	+30	+29	21	5.2	5.4	9.7	6.1	6	246
3,933	+30	+29	+29	+29	23	6.0	4.5	4.2	4.1	6	260
4,059	+30	+30	+30	+30	20	3.1	8.9	12.0	6.2	6	386
4,315	+30	+30	+30	+29	15	10.0	7.3	7.3	10.2	6	643

the effective contact time. It does, however, increase the vapor velocity. Steam is used at intervals to increase the activity of the clay.

Table 6 shows the results obtained through one complete clay cycle, covering approximately 11 months. All results shown are on sweetened samples. The "sun-color" test is made by exposing 450 ml. of the sample to 16 hours of bright sunlight in a clear-glass, round, pint bottle. The bottle is stopped with a cork stopper that has a 1/16-inch deep V-groove cut in its side over its entire length. A beaker is inverted over the bottle neck to prohibit the entrance of moisture and dirt. During the test the bottle is placed on a wooden platform, painted white. Note especially the uniformity of the color and gum test, as well as the stability on storage. The tests would indicate that the clay was still far from being

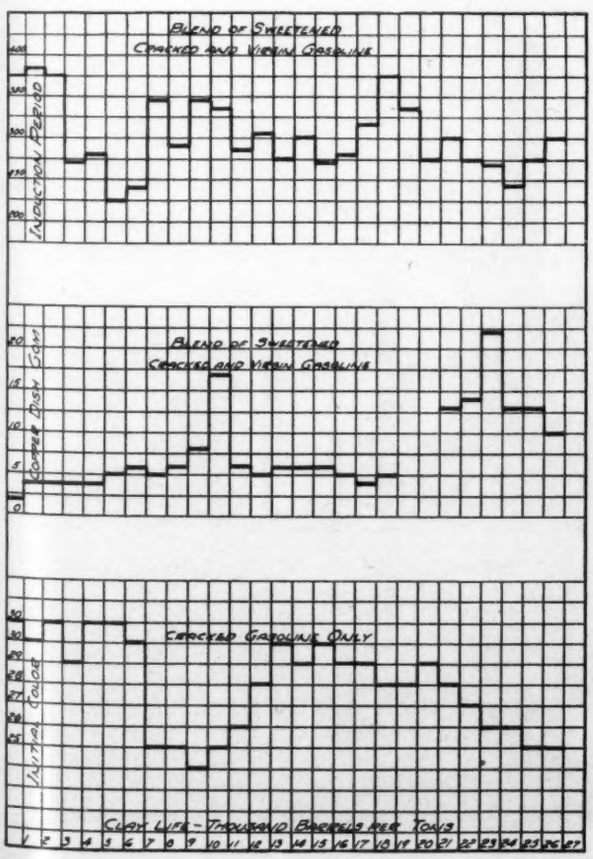

Blend of Sweetened Cracked and Virgin Gasoline
Induction Period
Blend of Sweetened Cracked and Virgin Gasoline
Copper Dish Gum
Cracked Gasoline Only
Saybolt Color
Clay Life - Thousand Barrels per Ton

FIGURE 3

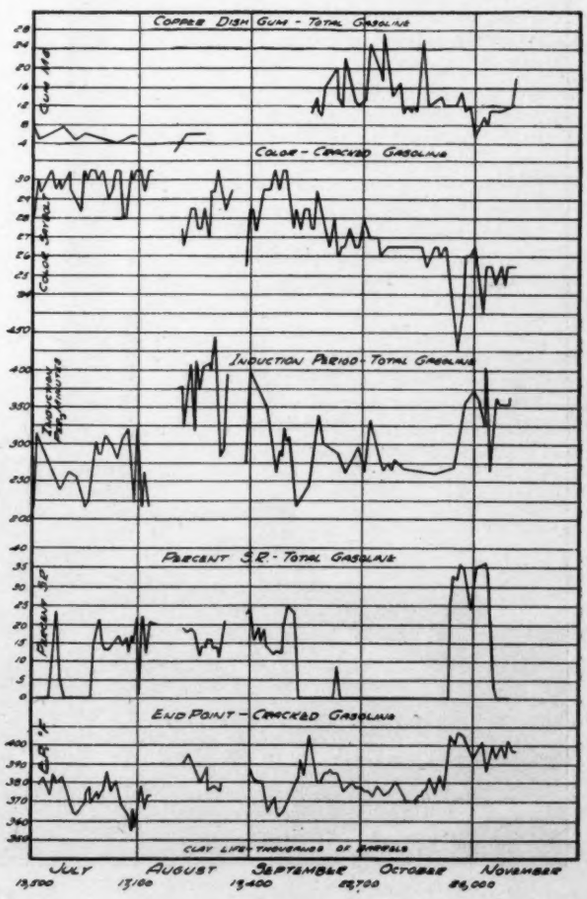


FIGURE 4

spent at the end of the run. It was, however, removed to allow inspection of the apparatus.

In view of the long contact time, coupled with a low rate as expressed in barrels per ton per hour, it is of interest to note that the amount of polymerization at the plant just discussed is not excessive. A check over an extended period showed that polymer-containing material drained from the unit at rates varying from 35 gallons to 113 gallons per hour, and ranged in gravity from 34 to 41° API. Total daily production was 27 barrels, of which 72 percent was naphtha boiling within the range of the gasoline being produced. This left a true polymer production of approximately 1.15 percent, based on the refined cracked gasoline. This figure is not out of line with results from other plants, which show polymer production as low as 0.5 percent and as high as 1.5 percent of the gasoline treated. It should be noted in this connection that, where clay towers have been installed in connection with cracking units which had been run for some time without them, there has been no evidence of decreased throughput or of decreased gasoline production upon the use of the Gray equipment—so that net polymer degradation is certainly below the error of magnitude of measurement of gasoline production. This is accounted for in part by re-cycling polymers to the cracking plant, and probably in part by conversion of some of the cracked gas to gasoline by catalytic action of the earth. It is understood that some plants have found a market for their polymers—which, in view of their many interesting properties, is not surprising.

TABLE 7

Operating Conditions and Reported Results

Charge to cracking unit	22-deg. API topped Kettleman Hills crude
Amount of gasoline, bbl. per day	427
Clay-treating pressure, lb. per sq. in.	40
Clay-treating temperature, °F.	350
End point of gasoline, °F.	400
Octane No. of gasoline, ASTM	68.5
Throughput, bbl. per ton	2,500+
Gum (copper-dish), milligrams	8
Color	30+

CLAY TREATING KETTLEMAN HILLS CRACKED GASOLINE

Before leaving the subject of clay treating cracked gasoline, reference should be made to a recent installation treating gasoline from topped Kettleman Hills crude. Two Gray towers are used, in series, each charging 7½ tons of clay and followed by a polymer separating tower. Table 7 shows operating conditions and reported results.

CLAY TREATING POLYMER GASOLINE

Although the discussion up to this point has concerned cracked gasoline, and the bulk of commercial

(*Continued on page 235*)

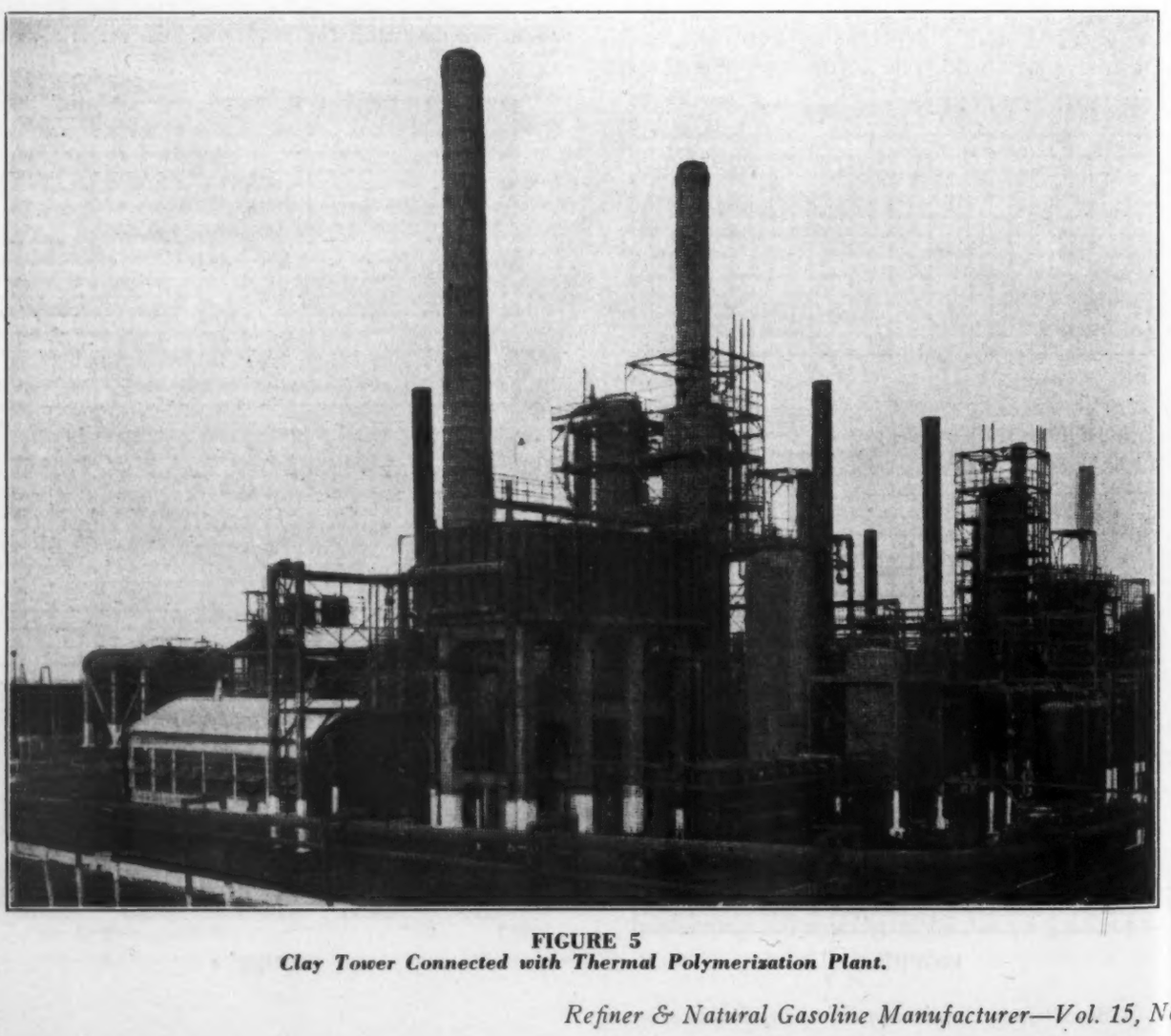


FIGURE 5

Clay Tower Connected with Thermal Polymerization Plant.

Instrumentation In Oil Refining

A. C. PROCTOR and GUSTAV EGLOFF
Universal Oil Products Co., Chicago

ONE of the important developments in the processing of oil has been in automatic control. This development has brought about marked economic savings due to producing better and higher yields of the more valuable products from the crude oil. Automatic control plays an important part in operating crude-oil stills, cracking units, and combined topping-cracking units which have been built in capacities ranging from small to large (up to more than 30,000 barrels per day of crude). At present an atmospheric distillation unit is being designed of a capacity of about 65,000 barrels of crude oil per day.

In the days of batch-shell still refining and cracking operation but a few years ago, a single mercury theremometer and an indicating pressure gage were deemed sufficient. The control of operation was by hand, with no automatic devices for determining fluid (liquid and gas) temperatures, pressures, flow rates, or liquid levels in the system. At the present time some refining units, in order to insure accurate control are equipped with more than 300 control or indicating points, which are serviced by highly-skilled instrument men.

From the time of mercury thermometers and indicating pressure gages to the present day, automatic controllers have developed so that they more nearly meet the requirements of modern refining. Refiners must increase yields and quality of products from their crude oil. Recovery of 100 percent of the crude-oil charge, with no loss, is ideal. With each plant going into operation, this ideal is nearer attainment; and instruments play their part. As refining has improved, controls have improved to meet modern requirements. Automatic-instrument developments have been effected to eliminate hand control and human frailty, thereby smoothing out operation and improving yields and products to meet present-day standards. Instruments have lessened the manpower required to operate a plant—thereby reducing cost. In addition, they are a check upon operation of units. One must be careful not to over-instrument a unit so that a false sense of security is manifested by its operator. He must still operate the plant. However, automatic controls are a help in that direction.

In refining operation, the variables entering into the processes are principally temperature, pressure, rate of flow, and liquid levels. These variables are interdependent, and a change of one affects the others. As a simple illustration: if the oil charge to the unit is increased without additional firing in the furnace, the transfer temperature will be reduced; therefore, the flow must be correlated with the heat applied. A unit should be studied thoroughly for all possible variations in different parts of the equipment, and automatic instruments should be used wherever applicable.

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 14, 1936.

THE accurate measurement of temperature in a refinery is of the first importance. From the time crude oil is measured in storage tanks and corrected to standard conditions of 60° F., its processing in the refinery to commercial products requires highly accurate temperature recordations.

Devices for measuring or controlling temperature are divided into the following major groups:

A. Expansion thermometers
B. Resistance thermometers
C. Optical pyrometers
D. Pyrometric measuring devices

A. Expansion Thermometers

Everyone is familiar with the garden variety of thermometer for temperature indication by means of the expansion of mercury, liquid, or gas. This is carried a step further by the use of the indicating-and-recording thermal-expansion type, with capillary tubing for remote reading. The expanding fluid may be liquid or gas. These devices have a definite top range at which accuracy may be relied upon. Maximum tubing lengths depend upon the type of thermometer. The expansion or contraction of the liquid or gas in the thermobulb, which is inserted at the point where the temperature is to be measured, moves a helical tube connected to a pen mechanism which records the temperature, or to a pointer which indicates it.

B. Resistance Thermometers

Resistance thermometers are of a class which depend upon the variation with temperature of the resistance of an electrical conductor.

All metals have the property of changing in electrical resistance with temperature. The most commonly-used metals measured by electrical resistance are platinum, nickel, copper, and iron wire because of their constancy at fixed temperatures after repeated coolings and heatings, and because of their relatively large change in electrical resistance per degree of change in temperature. Each of these metals follows definite resistance-temperature relations. For every degree of change in temperature, there is a corresponding change in resistance—the rate of change being termed the "temperature coefficient of resistance" of the wire.

A Wheatstone bridge is used for measuring the resistance of the thermometer by comparing it with the known variable resistance of one arm of the bridge. Resistance thermometers have the advantage of an accuracy of the order of 1-3 percent up to a maximum temperature of 1,100° C. (or 2,012° F.). They are important for laboratory work, where high precision is necessary. They are less important for refinery recordations; because bad contact, or a broken strand in a flexible cable, causes large errors. The relative fragility of this type of thermometer

necessitates very careful handling, and its calibration is easily affected.

C. Optical Pyrometers

Optical pyrometers utilize only the visible portion of the spectrum for temperature indications, and depend upon the eye for a comparison of the equality of two color images. True optical readings are made only under black body conditions; however, the radiant surface in the interior of a furnace under operating conditions may be assumed to have black body conditions, which introduces but a small error. A tungsten-lamp filament is placed in the plane of an image of the hot spot. The incandescent filament and the image produced by the lens are observed through an eye-piece. A small battery is used with a rheostat and with an accurate milliammeter. By means of the rheostat the current passing through the lamp is adjusted, until the brightness of the filament is equal to the brightness of the image produced by the hot object. When this point has been attained, the reading on the milliammeter is taken, and then compared with a calibrated chart for conversion to temperature. This type of measuring device is somewhat limited; since clear vision of the spot to be measured must be obtained, and any dust or smoke particles introduce inaccuracies. This type may be used at temperatures of 1,400° F. and above. In cases of high temperatures, say above 2,500° F., the intensity of the light through a lens is "too blinding"; to overcome this absorption screens are used, which reduce light from the hot body but do not affect the filament. A different calibration table would then be used to allow for screening.

D. Pyrometric Measurement

Pyrometers, both of the millivoltmeter and potentiometer type, play a very important part in reading temperatures throughout a refinery. A thermocouple placed at the point where the temperature is desired sets up an electromotive force which is measured in the instrument. The millivoltmeter type records this electromotive force by means of a sensitive D'Arsonval type of galvanometer. The potentiometer provides a means of opposing a known variable potential to the unknown electromotive force of the thermocouple.

In the early days, considerable difficulty was experienced with temperature-measuring devices. Thermocouples were continually burning out, or wells deteriorated. Consideration given to the nature of the gases in the combustion chamber of a furnace and to the materials chosen, will increase the life of thermoelements and wells to a large degree. The location of couples in a furnace has much to do with the type of thermocouple required. It is not always necessary to locate a thermocouple in the hottest spot of a furnace, as proper operating temperatures can be often established at a point of lower temperature.

TABLE 1

Type of Thermocouple	Usual Temperatures Ranges		Maximum Temperatures	
	(Deg. C.)	(Deg. F.)	(Deg. C.)	(Deg. F.)
Platinum-rhodium	0 to 1,450	0 to 2,650	1,700	3,100
Chromel-alumel	—200 to 1,200	—300 to 2,200	1,350	2,450
Iron-Constantan	—200 to 750	—300 to 1,400	1,000	1,800
Copper-Constantan	—200 to 300	—300 to 570	600	1,100

Thermocouples in commercial use, with their working-temperature ranges, are shown in Table 1.

Thermometers and pyrometers have been developed into controllers of high efficiency. To the system of measuring have been added electrical relays or mechanisms which control air to a diaphragm motor-control valve. Refinements give wide throttling ranges and automatic re-set for close temperature control.

Throttling range is the correlation of the pyrometer or thermometer and valve to provide the proper supply of controlled fluid such that the quantity of fluid is proportional to the deviation from the normal control point.

Re-set is the means of bringing the control point back to the desired operating temperature, within the throttling range of the instrument, for variations in the controlled flow. Instead of the control point moving within a fixed throttling range, it remains fixed and the throttling range moves about it.

FLOW AND MEASUREMENT OF FLUIDS (LIQUID OR GAS)

The volumetric measurement of fluids and their rate of flow in refining operations are fundamental factors in design and operation. These values must be determined as accurately as possible—not only by the engineer who designs the unit and by the instrument engineers; but operators should be thoroughly familiar with the importance of close control of fluid flows. The methods used in the refinery are:

A. Displacement meters
B. Differential-pressure meters
C. Pump-stroke counters
D. Tank gauges
E. Calibrated weirs
F. Calibrated lifting ball meters

A. Displacement meters record flow through a train of gears as a result of mechanical displacement of parts by the medium being measured. They have the following advantages:

1. Low first cost, especially in smaller sizes
2. Fair accuracy
3. Simplicity

They have the following disadvantages:

1. They record total flow, and not instantaneous rate of flow.
2. Mechanical wear causes expense for replacement of parts.
3. The volume range is limited, and cannot be readily changed.
4. They cannot be used on highly viscous fluids.

B. Differential-pressure-type meters are used widely in oil refining because of their inherent accuracy and flexibility. The usual commercial type of instrument consists of a metal U-tube filled with mercury, with a float transmitting the differential pressure to an indicating scale or chart. Another type utilizes a spring loaded diaphragm for measuring the differential pressure.

Differential-pressure-type meters use the basic formula:

$$Q = C\sqrt{h}$$

where:

Q=the rate of flow,
C=the constant dependent upon the physical characteristics of the differential-pressure producer, the physical characteristics of the fluids being measured, and upon the units used.
h=the differential pressure produced by the flow (usually measured in inches of water).

It is common practice to give the constant C for water or air flowing through the orifice under standard conditions. This water or air constant then is corrected for temperature, gravity, viscosity, and sealing liquid to give a constant for flow under operating conditions. For gas meters, corrections for atmospheric pressure, and for the static pressure in the line, must be made when calculating fluid flow.

The differential-pressure-type meters for different refining operations use for differential-pressure producers:

1. Orifice plate
2. Venturi tube
3. Pitot tube

AREA METERS

These devices all operate under the same principle, and may be differentiated one from the other by: *1. The orifice plate* consists essentially of a thin plate with a carefully-machined and -measured circular hole placed in the line through which fluid flow is taking place, and the differential pressure across the plate is measured by a manometer or differential gage; while the static pressure is taken by another gage. It measures the decrease in static pressure due to an increase in the velocity of the fluid stream caused by the known reduction in the cross-sectional area of the path of flow. *2. The Venturi tube* has a gradual change in cross-sectional area designed to give maximum pressure recovery. *3. The Pitot tube* measures velocity head, and usually consists of two tubes—one pointing upstream, and the other downstream.

The orifice plate (round hole, sharp edge) is the most widely used differential-pressure producer.

Advantages of the orifice meter are:

1. Low first cost
2. Adaptability to varying flow. (The size of the orifice may be changed, and a new plate provided, with little expense for different flow conditions.)
3. Relatively accurate when all factors are considered for free-flowing liquids.
4. Small space required in piping.
5. Ease of transmitting readings to a remote point.

Disadvantages of the orifice plate are:

1. Vaporization errors with highly-volatile liquids.
2. Lack of accuracy on highly-viscous materials.

A sample calculation of liquid flow through an orifice will be given to illustrate the factors involved. It is assumed that the size of the orifice has been determined, and that flow calibration is to be made under conditions as follows:

d=size orifice—1.250 in. (⅛-in. thick plate)
D=inside diameter of pipe—2.125 in.
T=temperature at orifice—675 deg. F.
Sealing liquid (glycerine, water, and alcohol), specific gravity of 1.000 (water at 60 deg. F.)
Pressure connections—in orifice flange
Viscosity, correction not used at 675 deg. F.
Gravity—20 deg. API at 60 deg. F.
$h_{max.}$=maximum differential range of meter—100 in.
Scale=0 to 10 square-root chart

Then:

$$C_w = 327.3 \times C_v \times d^2 \qquad (1)$$

where:

C_w=hourly water constant of the meter. (327.3 is a constant which embodies experimental and dimensional constant necessary to get C_w in gallons-per-hour units when a seal of specific gravity of 1.00 deg. is used.)

The seal correction for liquid or mercury is derived from the formula:

$$\sqrt{1 - \frac{\text{Sp. Gr. b}}{13.6}}$$

where
Sp. Gr. b=specific gravity of sealing liquid
13.6=Specific gravity of mercury
C_v=coefficient of velocity of the orifice, a function of the ratio of the orifice diameter to the pipe inside diameter, in inches for flange connections.

Then:

$$\frac{d}{D} = \frac{1.250}{2.125} = 0.588$$

From experimental data of well-known instrument makers C_v=0.653 for d/D of 0.588, using flange connections.
Then, substituting in equation (1)

$C_w = 327.3 \times 0.653 \times (1.25)^2$
=334 gal. per hour for one inch of water differential.

Then, multiplying by the square root of the maximum differential reading at the meter, and correcting the flow volume to 60° F., and correcting for gravity the maximum reading of the orifice meter is determined.

$Q_{max.}$=flow through orifice at the maximum reading of the meter in gallons per hour at 60 deg. F.

$$Q_{max.} = C_w \times \sqrt{h_{max.}} \times \frac{1}{E} \times \sqrt{\frac{1}{\frac{G}{E}}} \qquad (4)$$

Where:

C_w=water constant of meter
$h_{max.}$=maximum differential reading of meter
E=expansion, or ratio of hot volume of the oil to its volume at 60 deg. F. (Obtained from experimental data.)
G=specific gravity of the oil at 60 deg. F. (Referred to water at 60 deg. F.)

Then, substituting the quantities as given:

$$Q_{max.} = 334 \times \sqrt{100} \times \frac{1}{1.341} \times \sqrt{\frac{1}{\frac{0.9340}{1.341}}}$$

=2980 gal. per hour at 60 deg. F.

Since the meter is furnished with a square-root chart scale, the reading is proportional to the flow. Therefore, if the meter read 7.0, the instantaneous flow is:

$$Q = 2980 \times \frac{7.0}{10} = 2086 \text{ gals. per hour (volume at 60 deg. F.)}$$

If hot volume is desired, this flow is multiplied by the expansion E, or the quantity $\frac{1}{E}$ is left out in equation (4).

Gas-flow calculations are similar to this, except that the absolute pressure of the gas (static) is another variable, and the volume of the gas must be referred to a pressure base as well as temperature.

The Venturi tube is used mainly where high accuracy is desired. Volatile liquids tend to vaporize upon sudden changes of pressure or with turbulence, causing eroneous readings. With the Venturi tube, static pressure head is temporarily changed to velocity head with very little turbulence (or vaporization) and with almost complete pressure recovery farther down the line due to its streamline characteristics.

Advantages of the Venturi tube are:
1. High accuracy.
2. High-pressure recovery (low-pressure loss).
3. Ease of transmitting readings to a remote point.

Disadvantages of the Venturi tube are:

1. High first cost.
2. Exaggerated effect of viscosity changes. (The Ventrui tube is not practical for high-viscosity liquids for this reason).
3. Lack of flexibility for varying volumes of flow.

The advantage of the Pitot tube lies in its simplicity and ability to measure velocities in a conduit.

Area meters record or indicate the area of a variable orifice necessary to maintain a constant differential pressure across the orifice. They usually consist of a draw-gate which slides up and down to vary the size of a rectangular orifice to maintain the constant differential. The opening of the "draw-gate" may be calibrated in units to give rate of flow.

Advantages of the area meters are:

1. Ability to measure highly-viscous materials with fair accuracy. They can be used for asphalt, tar, or residuum, where other flow meters are useless.

Disadvantages are:

1. They are not useful for accurately measuring free-flowing liquids (of low viscosity).
2. Since moving parts are used directly in contact with the liquid, there is the danger of these becoming fouled by solids or change of viscosity of the liquid being measured.
3. Variation in viscosity affects measurement.

Differential-pressure-type meters adapt themselves readily to flow control as well as flow measurement. The manometer may actuate a control mechanism, which in turn actuates a control valve in the steam line of a pump, the discharge line of a pump, or in a speed-reducing coupling on a turbine-driven pump.

Flow-meter and controller readings may be transmitted to remote points by electrical systems. Orifice-meter piping may be run for a distance of 100 feet or so in a refinery to give remote reading and control.

C. Pump-stroke counters are used in determining pump displacement when corrected for volumetric efficiency of the pump and for temperature which gives the discharge volume. This method is not very accurate due to variations in pump slippage, vaporization, etc.

D. Tank gages are a reliable means of determining volumes, and are ordinarily used as standard. Volume in this case, as in the others, must be corrected to standard temperature of 60 deg. F.

E. The calibrated weir is an old form of measuring device which may have notches of different shapes. This is a combination area-head meter, both the area through which the fluid flows and the head causing the flow to vary at the same time. The measurement may be determined by a float gage, used with either indicating or recording mechanisms, or merely by a calibration on the side of the weir.

F. The lifting ball type of meter is constructed with a ball or plug located in a conical graduated tube mounted vertically with the inflow at bottom and the outflow at top. Gravity supplies the constant head or pressure differential; and, as the flow increases, the plug or ball increases its height, giving indications of flow.

PRESSURE MEASUREMENT

Pressure-measuring and -control instruments are used in refinery service for maintaining proper pressures on heating coils, vessels, and pumps—both as a matter of safety and as a matter of securing most efficient operation. Pressure instruments may be classified as follows:

1. Liquid-head, or manometer
2. Bourdon-tube
   a. Spiral form
   b. Helical form
3. Bellows
4. Diaphragm
   a. Spring-loaded
   b. Weight-loaded
5. Piston-type
6. Inverted bell

1. The liquid-head or manometer principle is used in the mercury barometer and the common U-tube. The rise or fall of a column of mercury is balanced by a pressure, until an equilibrium has been reached between the gravitational force due to the weight of the liquid and the force due to the pressure of the fluid whose pressure is to be measured. This principle is applied in the commonly-inclined draft gage, which is simply a glass U-tube filled with oil, with one of the legs of the gage inclined at an acute angle to the horizontal to spread the scale.

Some of the advantages of manometer-type gages are:

1. Ease and constancy of calibration.
2. Sensitivity at low pressures.

A few of the disvantages are:

1. The range is limited to comparatively low pressures, since the height of the liquid column is limited.
2. With the measurement of pressure of corrosive fluids, seals must be used, which involve calculations to obtain corrections. Seals must also be used at high temperatures.

2. The Bourdon tube is the most practical measuring means for high pressures. About the year 1849 Eugene Bourdon of France discovered that the free end of a bent, flattened, elastic metal tube would move when pressure was applied, either internally or externally; that this motion was directly proportional to the pressure applied; and that the tube would resume its original position upon release of pressure. The modern pressure gage utilizes this principle by transmitting the motion of the tube through linkages and gears to a pointer on a circular scale, or to a recording pen. The Bourdon tube may be made in a circular, spiral, or in a helical form to secure desired ranges or sensitivity.

Some of the advantages of the Bourdon-tube gage are:

1. The maximum pressure at which it is used is limited only by the strength and elasticity of the materials used.
2. It requires little attention beyond occasional checking and re-calibration.
3. It is rugged.

Disadvantages of the Bourdon-tube gage are:

1. Lost motion in linkage due to poorly-fitting parts or wear; causes a difference in reading on rising and falling pressure, which affects accuracy in some cases.
2. A change in elasticity of the metal used in the tube causes a change in reading which must be corrected at intervals.

As with other types of pressure instruments, the Bourdon tube measures the difference between atmospheric pressure and the pressure being measured. To obtain absolute pressure, barometric pressure must be added to the "gage pressure," as indicated by the gage, or the tube must be enclosed in a vacuum chamber.

3. The bellows type of pressure instrument is similar in theory to the Bourdon tube, and might even be classified as such. The pressure element consists of a metal cylinder with corrugations to allow elongation along the axis. This elongation is directly proportional to the pressure applied. The motion of the bellows upon change in pressure is transmitted to a pointer or a recorder.

4. The diaphragm type of pressure recordation utilizes the force due to pressure on a diaphragm as a measuring means. The diaphragm may be either "spring-loaded" or "weight-loaded." In the case of spring-loaded, the force on the diaphragm is proportional to pressure, and the elongation or contraction of a spring connected to the diaphragm is proportional

to the force exerted. The "weight-loaded" diaphragm measures the force by means of a weight and lever.

Diaphragm-type pressure instruments are not used often for pressure measurement in an oil refinery, but are extensively used to control pressure in the form of a diaphragm-pressure regulating valve. Such a valve is motivated by pressure variations on one side of a diaphragm in a chamber. The force of the pressure on the diaphragm may be balanced either by a weight or a spring.

A spring-loaded diaphragm connected to convey motion to a control valve is most commonly used. Pressure variations on the diaphragm cause the valve either to open or to close. By adjusting the tension of the spring, any desired pressure on the diaphragm may be maintained. By connecting the diaphragm chamber upstream from the control valve, "back pressure" is maintained—and the valve becomes a "back-pressure regulator." By connecting the diaphragm chamber down-stream of the valve, the valve becomes a "pressure-reducing regulator."

If a diaphragm has a pressure chamber on each side of it, with spring loading on one side only, it may function as a pressure-control valve to control a pressure differential between two points—with the valve opening or closing to maintain the differential desired.

Weight-loaded diaphragm valves are used in a similar manner as spring-loaded diaphragm valves to control pressure however, they require more space, and do not give as good service as the spring-loaded type. Weight-loaded types may be more sensitive at low pressures than spring-loaded.

Safety valves are a necessary precaution for the refinery in guarding against excessive pressure. They are of two types, viz.: the pop-type and relieving-type. The pop-type opens instantaneously and completely for full-relieving capacity when pressures are reached above those desired. The relieving-type is a gradual opening valve for temporary release at capacities dependent upon the rate or extent of excess pressure generation.

5. Piston type of pressure instruments operate by displacement of a piston in a cylinder due to pressure, in much the same manner as a diaphragm is displaced. The piston may be either weight- or spring-loaded. The chief difficulty in connection with this type is in avoiding leakage past the piston. When considerable motion of the piston occurs in measurement or control, the piston wears—causing leakage. For pop-tube valves, however, pistons are well suited since they are not required to move except in case of emergency. Piston-type instruments are subject to friction, and locking as a result of excessive friction must be avoided.

6. The inverted bell type of pressure instrument has some applications at low pressure. It consists of a cylinder with one end closed and the open end immersed in a liquid. Pressure applied on the inside of the cylinder causes liquid to be displaced, and the bell to be buoyed to a higher position.

Variation of the position of the bell with vacuum or pressure applied to the inside causes a pointer, recording pen, or controller to operate. The bell type of pressure instrument finds its main use on draft gages for furnaces, since it is quite accurate at low pressures and vacuum.

PRESSURE CONTROLLERS

By connecting any one of the types of pressure-measuring devices to a control mechanism, a pressure controller results. Variations in pressure cause the controller to actuate a remote valve by means of liquid pressure, air pressure, or electrical means.

The spring-loaded diaphragm type of regulating valve becomes a constant pressure-pump governor when the pressure chamber over the diaphragm is connected (through proper seals) to the discharge of the pump, and the diaphragm actuates a valve in the steam line to the pump. Throttling of the steam input controls the pump-discharge pressure.

Bourdon-tube mechanisms may close electrical circuits to operate alarm signals to warn operators of excessive pressures at important points in the refinery unit.

Deflection of a Bourdon tube as a result of pressure causes a mercury-tube switch to make contact, allowing current to operate a siren or "howler." At the same time that the siren operates, one of a number of lights is flashed to show, on the instrument-control board in the receiver house, the location of the excess pressure.

LIQUID-LEVEL CONTROLS

The control of liquid level plays an important part in oil refining in parts of the unit such as:

1. Separation of gases and vapors from liquids.
2. Separation of immiscible liquids, such as oil and water.
3. Insuring liquid level in vessels to maintain pump suction.
4. Prevention of accumulation of liquid in high-temperature vessels.

Two types of level controllers are primarily used in oil refineries—the manometer- and float-type. The float-type is the more widely used of the two.

The manometer type of level controller operates on the principle of a difference in pressuree between a liquid leg on the outside of the vessel and the head of liquid inside. A metal manometer, similar to that used in a differential-pressure flow meter, measures this pressure differential and controls in accordance therewith.

The float type of contoller may assume a number of forms. It may be mounted inside the vessel and connected to the control system through a rotary shaft with a stuffing box, or it may be mounted outside the vessel in a smaller vessel called a "float cage." The internal-mounting type is the least expensive of the two forms, especially when a manhole is available to attach the float from the inside. When this is the case, no special nozzles are needed on the vessel, but the controller may be mounted in a small pipe tap large enough to accommodate the shaft and stuffing box. The internal-float type is better adapted to wide variations in level.

In many cases "averaging-control" or throttling is desirable in a liquid-level controller. This type allows the level to vary within limits with minimum operation of the control valve, but does not allow the level to get beyond the limits set. This controller is useful where a smooth type of operation is desired without interference with other instruments, and when "cycling" or hunting is likely to occur with close level control. "Averaging-control" may be achieved by means of especially-shaped cams which cause the controller to function more vigorously when the level approaches the limits decided upon, but minimize the amount of control when the level is within the high and low limits set by the operator.

Remote level controllers transmit impulses to the control valve by means of air lines or, in some cases, by electrical means. Valves may be at a point remote from the controller with this type. Direct-connected level controllers operate with the float motion trans-

mitted by levers and rods (or chains) to the control valve. The valve must be mounted almost directly above or below the controller, and does not operate very well at great distances from it.

Interface-liquid level controllers are used when two immiscible lquids, usually oil and water, must be separated. A distillate receiver for steam-distilled gasoline is an instance in which an interface controller is useful. The float ball in such a case would be balanced to cause it to sink in gasoline, but not in water. The float actuates a valve in the water drain from the receiver, causing the valve to open when the water level rises; but is unaffected by a change in gasoline level. Another controller is used to control the gasoline level.

Frequently level indication, rather than control, is desirable. Gage glasses are not desirable in most cases of high-temperature operation, and may also become fouled upon exposure to "dirty liquids." Level indicators may be of the float-type, or the manometer-type, with the reading transmitted electrically or by piping to the instrument board. In some cases, level recorders are used.

An excellent way of transmitting level indications is by means of electric lights. With this system, the float actuates rotary or mercury-tube switches to cause colored lights to show the fluid-level limits on the instrument board. By having one light for high and one light for low, with normal levels, and by having two lights on at a time for intermediate points, five level positions can be indicated by the use of three lights.

In many cases the use of a level controller with a valve in the steam line to a pump or in the discharge line acts as a flow controller, when other conditions remain constant, and when the pump draws suction from or discharges into the vessel in which the float is located.

CONTROL VALVES

Without careful design of control valves, the best of controllers could not function properly. A control valve must have desirable flow characteristics, be designed to withstand pressure, temperature, corrosion, erosion, and be free from excessive friction and from a tendency to become fouled by coke or asphaltic material.

Improvements in various factors which influence controllers have been made through suggestions and willingness of refiners to install instruments on trial. Instrument characteristics, as well as those of valves, have been changed to meet certain requirements as a result of experience in operation. Proper relation between the instrument and the valve has been worked out for better correlation. A firm of consultants in oil refining have an experimental unit in which developments along this line have taken place. For example, on a chamber draw-off line, where the temperature ranged from 880° F. to 920° F., the upstream pressure being from 200 to 475 pounds per square inch with a downstream pressure of 75 pounds per square inch, considerable trouble was experienced from coking, sticking of the valve, breakage of the stem, and burning out of the packing. The plugs, seats, rings, and any part of the valve coming in contact with the flow were streamlined to overcome coking. The stem was extended and ball-bearing guides used to prevent stickiness, and an air-cooled packing box was so arranged as to eliminate burning-out of the packing. Erosion and corrosion were prevalent, and this was overcome through the design and the materials used. This valve was handling a mixture of gas, gasoline, and residuum. Today the development is such that this is no longer considered a major problem.

Control valves may be actuated by different methods. They may be opened or closed directly by a float, by an electric motor, by a solenoid electro-magnet, by hydraulic pressure, air, gas, or steam pressure on a piston or diaphragm. For oil-refinery work, the use of air-operated diaphragm motor valves has been most common.

The diaphragm motor-control valve consists of a globe or angle valve, the plug of which is raised or lowered by means of air pressure on one side of a diaphragm and spring pressure on the other. The degree of opening of the valve is varied by changing the air pressure on the diaphragm. As a rule, the most desirable flow characteristic of the valve is that in which the open area varies as the square percentage lift of the valve plug. To achieve this type of flow, two types of plugs are used—the V-port, which is a sleeve-valve type of construction, with triangular shaped openings or ports; and the parabolic plugs, which is similar to the ordinary globe valve, except that the plug is machined to give the proper parabolic flow characteristics. Double plugs are most common, although a single plug may be used. Single-plug control valves require large-diameter diaphragms for exerting sufficient force to move the plug.

The following formula is used in determining the size of the control valve which is used to control liquid flow:

$$d = \sqrt{\frac{Q}{K}} \times \sqrt{\frac{G}{H}} \qquad (3)$$

where:

d = nominal valve size, in inches.
Q = flow of liquid (hot volume), in gallons per minute.
K = a constant.
G = flowing specific gravity of the liquid.
H = differential pressure across the valve, in lb. per sq. in.

Let us suppose a valve is to handle 100 gallons of liquid per minute (volume at 60° F.) of 30° API 0.9340 specific gravity (at 60°), with the upstream pressure on the valve 100 pounds per square inch, when the temperature of the liquid is 500° F. A common value for K, for liquids, is 10 (although the value of K varies with valves of different construction, and must be determined for any line of valves).

It is desirable to have a differential pressure across the valve such that the valve, and not the line resistance, is in major control of the flow. Let us assume in this instance that $H = 25$ pounds.

Then:

$Q = 100 \times$ expansion of 20-deg.-API oil at 500 deg. F.
$= 100 \times 1.24$
$= 124$ gal. per min., hot volume

$$G = \frac{0.9340}{\text{Expansion}}, \text{ or } \frac{0.9340}{1.24}$$

$= 0.753$ hot specific gravity at 500 deg. F.
$H = 25$ lb. per sq. in.

Since the *normal* flow is 124 gallons per minute, the valve may be designed for a *maximum* flow of 248 gallons hot volume. (This will depend upon the system.)

Substituting in equation (3):

$$d = \sqrt{\frac{240}{10.0}} \sqrt{\frac{0.753}{25}}$$
$$= \sqrt{4.31}$$
$$= 2.08 \text{ in.}$$

Since doubling the normal flow to get maximum flow was somewhat arbitrary, the next lowest nominal valve size, 2 inches, would be used in this case—although, as a rule, the next largest size is used.

Gas and vapor flow-valve sizes are calculated in somewhat the same manner, but they are slightly more complicated—and will not be described here.

In designing control systems, it is good practice to allow a substantial ratio of pressure drop across a control valve to that in the connecters system (from 100 to 200 percent of the line resistance or friction drop); since a control valve provides more effective control under these conditions.

When throttling control is not desired, the ordinary disc type of plug is to be preferred to the parabolic. In cases where a valve opens to allow steam to a turbine-driven centrifugal pump, in case of failure of a motor-drive, the parabolic flow characteristics are unnecessary; since the valve is either fully open or fully closed. In cases where valve lift is small, as on a pump-pressure governor, disc-type plugs are used.

SPECIFICATION OF OPERATING CONDITIONS FOR CONTROL INSTRUMENTS

It is highly important that the instrument manufacturer know as closely as possible the operating conditions under which his equipment must work. The following will serve to illustrate how these are supplied in refinery design.

In the case of a temperature controller with the valve in the steam line to a pump, the following conditions must be known:

Location of bulb.
Length of capillary tubing.
Type and size of pump.
Suction pressure, in pounds per square inch.
Discharge pressure, in pounds per square inch.
Steam pressure, in pounds per square inch.
Exhaust pressure, in pounds per square inch.
Control operating temperature—minimum-normal-maximum.
Quantity of heating or cooling medium at 60° F.
  Minimum, in gallons per minute.
  Normal, in gallons per minute.
  Maximum, in gallons per minute.
Flow temperature of heating or cooling medium.
Gravity of heating or cooling medium at 60° F. API gravity.
Special conditions: (if any).

For pressure control with the control valve in a gas line, the following conditions must be known:

Location.
Line size, in inches.
Gas flow at 14.7 pounds absolute and 60° F.
  Minimum, in c.f.h.
  Normal, in c.f.h.
  Maximum, in c.f.h.
Up-stream pressure, in pounds per square inch—minimum-normal-maximum.
Downstream pressure, in pounds per square inch—minimum-normal-maximum.
Differential pressure, in pounds per square inch—minimum-normal-maximum.
Flowing temperature, in °F.
Specific gravity of gas at 14.7 pounds absolute and 60° F.
Special conditions: (if any).

For flow control with an orifice plate or Venturi tube in the discharge of a pump and the control valve in steam line to pump, the following conditions must be known:

Pump; size, type, etc.
Size line at orifice, in inches.
Flow, at 60° F.
  Minimum, in gallons per minute.
  Normal, in gallons per minute.
  Maximum, in gallons per minute.
Flowing temperature, in °F.
Viscosity at flowing temperature, in seconds (Saybolt Universal).
Gravity of flowing liquid, at 60° F., in degrees API.
Suction pressure, in pounds per square inch—minimum-normal-maximum.
Discharge pressure, in pounds per square inch—minimum-normal-maximum.
Differential pressure—minimum-normal-maximum.
Steam pressure, in pounds per square inch.
Exhaust steam pressure, in pounds per square inch.

For level control with the control valve in the steam line to a pump, the following conditions must be known:

Location.
Valve line size, in inches.
Pressure in vessel, in pounds per square inch.
Gravity of oil in vessel at 60° F., in degrees API.
Temperature of oil in vessel, in °F.
Pump size and type.
Quantity of oil pumped at 60° F.
  Minimum, in gallons per minute.
  Normal, in gallons per minute.
  Maximum, in gallons per minute.
Temperature of oil pumped, in °F.
Gravity of oil pumped at 60° F., in degrees API.
Pump-discharge pressure:
  Minimum, in pounds per square inch.
  Normal, in pounds per square inch.
  Maximum, in pounds per square inch.
Pump-suction pressure:
  Minimum, in pounds per square inch.
  Normal, in pounds per square inch.
  Maximum, in pounds per square inch.
  Pump-differential pressure:
  Minimum, in pounds per square inch.
  Normal, in pounds per square inch.
  Maximum, in pounds per square inch.
Steam pressure in pounds per square inch in °F. (total temperature or super-heat).
Exhaust-steam pressure, in pounds per square inch.
Rising float to (open) or (close) valve.
Special conditions (corrosion, etc.)

The foregoing conditions required to determine type, range of controller, and valve sizes illustrate what is required in installing controllers. It must be remembered that the purpose of other controls are not to be interfered with. For every process, there is one best set of conditions.

SERVICING OF INSTRUMENTS

As instruments in a plant play such an important part in respect to processing, it is natural that efficient instrument men are employed for servicing and for ironing out any difficulties that may be encountered, as well for calibrating and adjusting the instruments as a matter of daily routine. This requires trained men with a complete knowledge of the process as well as proper training in the field of instrumentation.

The success of an instrument in commercial operation depends upon the skill and ability of the plant instrument man, whose aim should be the accuracy of measurement and control. Errors in instruments are costly, as they result in lowered yields and lowered quality of products, and create a hazardous condition. Studies of the record or indication of instruments should picture to the instrument man's mind whether or not all is well. His sense should be an anticipatory one. He should be so familiar with his instruments that trouble can be eliminated before anything of serious consequence takes place. When trouble occurs, the instrument man will find that his skill and experience will be the determining factors as to whether or not shutdown may be avoided. This indicates his importance in a refinery.

It can be appreciated that in small refineries the operator must service the instruments; therefore, it is well to have the operator trained along these lines.

Controlled Disposal of Wastes vs. Pollution

W. B. HART
The Atlantic Refining Company
Philadelphia

"CONTROLLED disposal of wastes vs. pollution" is a phrase that aptly fits a situation confronting many sections of the country. This situation has been growing in importance for many years, but recently has taken on particular interest because of its relation to other problems involving natural resources—such as soil-erosion control, reforestation and flood control.

Whereas flood control has to do with establishing uniformity of the quantity of water flowing into our streams, "waste disposal vs. polution" is concerned with the quality of our water resources.

Natural lake and stream waters, subject to natural conditions only, contain widely-varying quantities of organic and inorganic material in suspension and in solution. This has always been so. Yet these waters have utilitarian value. In some cases they are safe for drinking—the highest value in water use. But today no one, except in rare cases, can drink from a spring or stream without fear of water-borne disease. In other words, one would fear that some contamination had destroyed this particular utilitarian value. From this we can develop a definition for both sides of the situation: "controlled waste disposal vs. pollution." Where the utilitarian value is not destroyed even in using the drainage value of our streams, we have the picture of controlled waste disposal. Where wastes are indiscriminately dumped into lakes and streams, beyond the ability of these waters to handle them, the utilitarian values are destroyed, or made difficult and expensive to recover. Such is pollution in the problem of today.

This paper was presented at Sixth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 14, 1936.

HOW POLLUTION STARTS

A DEPRESSION in the earth's surface, similar to a gulley, ranges down from the higher country to the sea. Some water is flowing down the course of this depression, and other similar water courses join it along the way. All this is of no consequence.

Now let us put some grass, brush, and trees along the stream, and a good road beside it. Soon motorists are using the road and enjoying the scenery. Put some fish into the stream, and more motorists drive out to catch them. These things are important, but not essential.

Now let us put a farm on the banks of this stream, a truly agricultural enterprise. On the opposite bank let us put a stock farm. Both of these endeavors are possible because of the stream. It supplies water for the farmers, the crops, and the stock. True, the wastes from these farms are drained to the stream, but natural processes within the water soon render these wastes innocuous. Here, too, the stream is useful. It drains the district.

To this attractive region an industry moves, and with it comes population — as operators and their families. This industry and village enjoy all the benefits of pure water. They prosper. Our stream has taken on new importance. Not because it is a stream, but because it continues to supply good water and continues to digest and carry off the wastes. But it requires more run of stream to do this, and also some preparation of its waters before use. Yet, on the whole, the community is a thriving one, and its advantages become a by-word.

More industries and more people become established along the stream; and eventually, either as a result of epidemic or interference with industrial processes, it is realized that its waters no longer have their original value. It cannot supply the domestic water needs of the community; it makes the cattle sick; it discolors and kills vegetation and the trees along its banks, and must be treated by expensive processes for use in manufactures or in boilers. Pollution has arrived. The farmers move away; the scenic effect of the region is lost, and motorists no longer use the road as a drive or come out to fish. Recreational uses of the water are not safe, and pleasure or commercial fishing is ended. There is left only industrial use of the water (at a cost) and navigation. For domestic supply, the people have a choice of paying for expensive treatment or expensive installations to bring water from a distance.

Now, following this history just a little further, let us watch the banks of this stream as the vegetation and trees are killed. With each rain storm gulleys form, and soil and silt are washed into the stream bed. It becomes shallow, and shoals form. Navigation can only be continued by the expense of dredging. At times of heavy storm, run-off from denuded areas becomes greater, and the shallow stream bed will not carry the water. The result is flood, with the accompanying damage to property and possible loss of life.

This is pollution. It is aided by other natural forces, but in itself it is a major contributor—all because of a lack of foresight, even when the conditions in early stages of the situation pointed the way. By control of waste disposal, the dire picture just described could have been prevented, in large measure, if not entirely.

CONTROLLED WASTE DISPOSAL

Let us examine this idea of controlled waste disposal to see what it means. To do so we can use the stream just described and follow its history, starting with the advent of industry and population.

Our first assumption will be that there is a definite will to protect this stream, not necessarily for the sake of the stream, but because of its values that

can be harnessed and made use of, similar in idea to making use of water power. To do this the stream must be studied; its flow determined—maximum, minimum, and average; its water analyzed to learn its nature and its capacity to assimilate wastes. With these data at hand, the wastes of the community — both domestic and industrial — are next studied, and the demand upon the stream that each will make established.

Without going into further detail, the demand for disposal will be set up against the capacity of the stream to handle it, and a balance struck to show just how much assistance will be required by the stream in carrying out its drainage function. The disposal of all wastes would be handled through predetermined treatment processes to keep within this limit. Therein lies the control. It does not mean the conditioning of all wastes to the purity of potable water. It means only helping the stream to do what it will always do if given a chance. Natural laws will work just as effectively for us as they will against us. It is only a matter of condition in the stream as to which way they turn.

With the wastes of the community controlled in quality or quantity before disposal, the farms of our pictured region will continue to prosper; the motorists will continue to enjoy the scenery along the road, and may stop to catch fish; the mills and community will have a good water supply; and the people, in their increasing leisure hours, will have recreation almost at their door. There will not be the pristine purity of the days prior to the coming of the first farm. There will be some change in condition. But by far the major part of every item of stream resource value will be retained even at some cost in money—this in comparison with cost and no resource value where pollution has taken control.

THE ECONOMIC PROBLEM

Again returning to our original phrase: "controlled disposal of wastes vs. pollution," it is worthy of examination in another light. What does "controlled disposal" cost, and what does pollution cost?

Going back 25 of 30 years, who would set up a money value on the waterway resources of the nation? They were of almost inestimable value. Consider the earnings they have made possible in that length of time. Those earnings are rapidly being reduced by the cost of handling polluted water, until today our water resource value (though still great) is shrinking rapidly. It costs too much to recover.

No real estimate of the cost of pollution has ever been attempted. An approximate estimate can be made and—without going into the detail of treating water for various uses, installations for distant supply, cost of destroyed industry, corrosion, dredging of shoals, etc.—this estimate runs from $300,000,000 to $500,000,000 annually. This is an estimated figure, and is based on rather meager information; but even so, the final figures resulted even after downward revisions to assure conservatism.

Compare the figure with soil-erosion cost estimates. Water- and wind-erosion each year are carrying 3 billion tons of soil beyond use. Already, 100 million acres, equal to the area of Illinois, Ohio, Maryland, and North Carolina, have been destroyed. Another 125 million acres is seriously impaired, and another 100 million acres of the finest agricultural land is menaced. The annual cost to the nation is estimated at $400,000,000. The accumulated cost so far is figured at about 10 billion dollars. It is further estimated that if preventive measures are not taken, the cost will mount to 25 or 30 billion dollars within the next 50 years.

Pollution and soil erosion are comparable economic problems; and the ever-mounting cost of pollution, resulting from increase in population, industry, and the ravages of other natural forces, will rapidly become unbearable.

It may well be asked: "What can the control of waste disposal do for us?" This may be answered by saying that proper control will bring back, in large measure, the streams that have been ruined. It will also retain the resource value of those lakes and streams that have not lost this value. It will not restore the pristine purity of years ago. It will not cause salmon and shad to return to streams from which they have been driven. Other changes in other natural forces must take place before such things can be accomplished, and this is unlikely. Of most importance is the fact that all users of water will have that use at the least possible expense commensurate with other requirements for successful operation—and not the least of these requirements is public good will.

Users of water have learned much about preparing it for various types of consumption. With the control of waste disposal, treatments would be required in much less degree. This would be the contribution of domestic and industrial waste disposal. The producers of wastes would treat them so that the available knowledge concerning the preparation of water for its various uses would be fully adequate and leave a safe margin. This would be the contribution of the users of water.

REFINING AND POLLUTION

In some sections of the country petroleum refining has been mentioned as one of the "four horsemen of pollution." This was several years ago. Since that time there has been considerable improvement. Also, since that time, the agitation by the champions of clean streams has increased many-fold. The subject is a popular one. It has political value, and much prestige will accrue to the individual who will bring about legislation that allegedly will solve the problem. This is evidenced by the fact that today 12 bills are printed and under consideration at Washington. If in each case these bills were companion bills, there would be 6 separate and distinct proposals. This is the greatest number, by far, that has ever been introduced at any one session of Congress. Some would work untold hardships on industry; others are unworkable; and some merely call for investigation. Several theories of administration are involved. States' control vs. federal control is not the least important among these.

In any event, petroleum refining is vitally interested; for petroleum refining uses large quantities of water and must dipose of wastes. Has the petroleum industry as a whole had the foresight mentioned in connection with our previously-pictured stream? There is reason to believe that it has not. Some refineries have gone to considerable trouble to protect the quality of the waters into which their wastes are discharged. This has been the case in some instances when the water receiving the wastes has been already badly polluted; but the industry as a whole, large plants and small, has not had such

foresight. As a rule, it has been only under threat from authorities that action has been taken. This has been true of other industries as well, and also of municipalities.

There are several reasons for this. Custom, for instance, is one reason. For years back people have used the streams to get rid of their wastes. They became used to doing so, and have continued to do so regardless of effect.

Then there has been ignorance of the effects of wastes on the waters receiving them. There are those who do not realize that these discharges are harmful to the water quality.

Also, there are those who realize that they are causing trouble but cannot help themselves, either from lack of funds or because there is no way known for handling the wastes and eliminating their noxious characteristics.

But there are those who know how to control their waste disposal—or at least could readily get the information—and who are not short of funds, who yet continue to destroy the resource values of streams either because, as they say, the other fellow hasn't done anything about it and if they did something, it would place them at a disadvantage; or because they just don't care how much they invade the rights of others.

LEGISLATIVE PROBLEMS

Now let us examine these reasons, bearing in mind that they apply to all industry, and to towns and cities as well, and try to figure out whether we are ahead or behind in the game. Then let us narrow this down to the field of petroleum refining.

First, take the discharge of wastes in the light of its being the customary things to do. It has been shown that there is not particularly serious result from this as long as the utilitarian values of the waters—the resource values, if you please—are not destroyed. But in a large percentage of our total waters some of these values have been destroyed, and it is costing the country a lot of money, and industry in particular a lot of good will. This also applies to those who are ignorant of the harm they are doing. Ignorance of the law is no excuse. Defiance of natural laws, either in ignorance or otherwise, gives you even less chance. Nature's court does not recognize technicalities.

Consider the reason designated as lack of funds—a reason that in some instances is sound, and in others not so sound. This reason has been weakened by investigations revealing many instances of unwise expenditures wrecking the financial position, particularly of municipalities. In the same way an examination of the plea that there is no known method for handling the particular waste may show that no particular effort has been put forth to find a method. In some instances, however, this plea is absolutely sound.

Now, both these reasons have been highly emphasized, and the result has been that legislation is proposed to correct the matter. Both present ways to spend money—a more or less national pastime. But the federal-loan-and-grant idea is tied in with a lot of other conditions that would not be so acceptable. The ultimate result has been that these reasons have been made an argument for federal control of the problem.

Let us now consider the reason most frequently advanced by industry for objecting to pollution-control legislation in various states. That reason is that, although they know what to do and have the funds to do it, the added burden would be a handicap in competition where competing plants were in different states. The logical conclusion from this is that the state is an inadequate unit for attack upon the problem. Those interested in pollution-control legislation did not miss this conclusion, and industry's own reasoning became the best weapon of its opponents for advancing legislation based on federal control. Without going into a discussion of states' rights vs. federal control, it can only be said that industry was put in a rather peculiar position in having to defend itself against attack with its own weapons.

Now let us look at the position of those who do not care, and see what they have contributed. Can you imagine what would be the effect on their sales if they were confined to a local market, and it was advertised in the local papers that they were ruining a water supply—or, at least, making it more expensive for the people in the community; or that they were ruining recreational facilities, etc.? That sort of advertising is going on every day. The particular plant or concern may be affected only slightly; for they may market very little locally. The advertising does not mention names either; and, as a result, the blame is saddled onto the entire industry—carrying with it the public ill will and an eagerness for any anti-pollution legislation, no matter how prohibitory.

The position of industry as a whole may be summed up by saying that it has made itself a lot of trouble; it has taught many things to those who, though sincere, lean toward the impractical and prohibitory; it is bearing the burden of blame for all pollution, since that from domestic sewage, although it constitutes possibly 75 percent of the total, is not much advertised. Industry is the target of public ill will, and is gradually being driven into a corner by legislative schemes—one of which sooner or later will very likely become a law. Unless industry can stand up and demand a voice in creating the rules under which it must play, considerable cost and inconvenience may come to some—and some may come to all.

To be in this position industry must enter the field with clean hands, and to do this it must clean house. In this effort it must have leadership—someone who will make the start, who is well equipped with knowledge of what to do in controlling the disposal of its wastes. There are two very important reasons why the petroleum-refining industry is the logical one to take this position. It is a large user of water, and it has studied its wastes probably more completely than any other industry. For the past six or seven years the American Petroleum Institute Committee on Disposal of Refinery Wastes has been hard at work on the subject, and has published adequate procedures. They are not simple panaceas; some judgment is necessary in their application.

There are probably three or four major wastes to consider. They are waste oils and emulsions, waste caustics, acid waters, and acid sludges. If the disposal of these four wastes is well controlled, any stream receiving the resultant waste water will have ample opportunity to retain all its value. In most

cases the cost of such control will be surprisingly small; particularly will this be a surprise to those who have not bothered to look into the subject.

There will be a return on the investment as well. In some cases this will be in actual saving of materials or recovery of useful by-products. There will be the return from greater efficiency from a well-kept house; but, most of all, there will be the value of public good will and the effect on other industries. Anticipated resentment will not materialize. There is too much to be gained by going along with the leader. The greatest voice in rule-making will go to him who makes the greatest effort at following the rules. It is bound to, for he will have the most experience and will be listened to. And in the end there is the saving to the nation of the cost of water pollution. All that is required is the will to make the start. That particular commodity can only come from within the individual elements of the industry.

The old cry of "catfish or commerce" is costing us money. It must be changed to "catfish and commerce," either by ourselves or by those who will not look upon our problems with the same sympathy. The law of averages has been well established. Undesirable legislation has failed of enactment on several occasions, but we should bear in mind that playing a fiddle did not stop the burning of Rome.

Clay Treating of Motor Fuel

(*Continued from page 224*)

clay treating has been with cracked gasoline, this treatment is applicable to other motor-fuel products as well. A notable instance is motor fuel produced from gases by polymerization. Here the material to be treated is high in octane value, and a process which can refine it with minimum loss and full retention of anti-knock properties is, of course, to be favored. Both the Osterstrom and the Gray processes are being used for this purpose. In the application of the former, and in some of the latter, the polymerized gasoline is blended with cracked products before being clay-treated. In at least one plant, however, a separate Gray-tower installation is used, and results on polymer gasoline are available. The polymerization unit, of the thermal type, has already been described.[11] Figure 5 shows the clay tower and polymer separator. Operating results are abstracted in Table 8.

In addition to the application of clay treating to cracked and polymerized motor fuel, laboratory and pilot-plant investigation has shown that it is adapted to the refining of motor benzol. However, no commercial installations have yet been made.

TABLE 8

Clay Treatment of Polymer Gasoline

Size of tower, ft.	10 x 40
Clay capacity, tons	18
Gasoline, bbl. per day (gross)	1,100
Gasoline, bbl. per day (net make)	700
Clay-treating temperature, °F.	330
Clay-treating pressure, lb. per sq. in.	25
Color before clay tower	dark straw
Color after clay tower	dark straw
Color after polymer separator	27
Gum (copper-dish), milligrams	20 to 40
Induction period,* min.	120
Induction period plus 1 lb. b.a.p. per 100 bbl., min.	240+
Octane No., ASTM	79
Clay life, bbl. per ton	20,000

* Bomb method.

COSTS

It it difficult to generalize concerning the cost of clay treating. Major operating items are capital costs, due to the installation, and cost of clay. Those in turn vary with the conditions. Gray-tower installation costs depend on the size and number of towers, working pressure, refinery requirements as to construction, etc. Some installations, made from existing vessels at low cost, have run as low as $12 per-barrel-per-day capacity. Some, where complete engineering was necessary, have cost more than $30 per barrel per day. Most installations which have been made are in the $15-$25 per-barrel-per-day range. Based on long experience of one refiner, all direct operating costs—including clay, clay handling, steam, etc.—aggregated less than $0.01 per barrel at 2000-barrels-per-ton throughput—a clay life well below what most plants are obtaining. Assuming a cost of $20 per-barrel capacity for the installation, and a 20-percent-per-annum write-off, the following figures are obtained (omitting license fees):

	Per Barrel
Installation	$0.011
Operating costs	0.01
Repairs and maintenance	0.002
Total	$0.023

These figures are conservative. Clay costs are frequently less than ½ cent per barrel. The repair item set up is liberal. Sweetening costs are not included; since they are inherent, whatever the refining method, when a doctor-sweet product is required. Any method applicable to sweetening cracked products may be used. Doctor treating, in the conventional manner, was almost universally relied on until quite recently; but in the past few years modifications of this method and others, such as those utilizing copper chloride, have been used with considerable success.

BIBLIOGRAPHY

[1] T. T. Gray and M. R. Mandelbaum, *Ind. Eng. Chem*, 16, 913 (1934).
[2] T. T. Gray, U. S. Pat. 1,340,889.
[3] T. T. Gray, U. S. Pat. 1,759,812, 1,759,813, 1,759,814, 1,908,599, etc.
[4] R. K. Stratford, U. S. Pat. 1,768,342.
[5] M. B. Cooke and A. W. Hayford, *Refiner*, 13 [3], 83 (1934).
[6] J. C. Morrell and G. Egloff, *Oil Gas J.*
[7] M. R. Mandelbaum, *Proc. World Pet. Cong.* 2, 21 (1933).
[8] T. H. Rogers, J. L. Bussies, and J. T. Ward, *Ind. Eng. Chem.*, 25, 397 (1933).
[9] H. M. Steininger, *Ind. Eng. Chem.*, 26, 1039 (1934).
[10] R. H. Price and P. L. Brandt, *Oil Gas J.* 35 [45], 54 (1935).
[11] P. C. Keith, Jr., and J. T. Ward, *Proc. A. P. I.* 16 (III), 129 (1935).

Natural Trends . . .

T. W. LEGATSKI
Phillips Petroleum Company

Before the Fifteenth Annual Convention of the Natural Gasoline Association of America, Tulsa, May 14, 1936

FROM a purely technical viewpoint the product of the natural gasoline industry is not natural gasoline. It is volatility. Therefore, when we speak of "Natural Trends" we must automatically take into account all of the sources of volatility regardless of the specific terminology employed. The object of this paper is to bring up to date our information on the volatility trends of motor fuel and also to show the relatively small part played by natural gasoline in this changing picture.

In a paper presented before the Association one year ago by Oberfell, Alden and Trimble,[1] the volatility trends of motor fuels for the period of 1929 through 1934 were illustrated in a number of ways. It will be recalled that their paper dealt with the results of a comprehensive survey of fuels marketed in the central states. Samples were obtained periodically from 16 key cities. The test results were interpreted by applying tax return information to arrive at the weighted average quality. In substance, the conclusions reached as a result of their study were:

(1) That the volatility of Mid-Continent motor fuels as reflected by vapor pressure and distillation characteristics had increased appreciably over the period.

(2) That the increase in volatility had occurred almost in the same degree in each of the three grades of fuel. The increase was not limited to winter fuels.

(3) That the greatest change had occurred in the region of the 50 percent and 90 percent distillation points.

(4) That the spread between the characteristics of extreme types of fuels had remained substantially constant throughout the five-year period covered by the survey.

(5) Other data available to the authors indicated the trend in quality was not limited to Mid-Continent fuels but applied in a lesser degree to all parts of the country.

[1] Oil and Gas Journal, July 4, 1935.

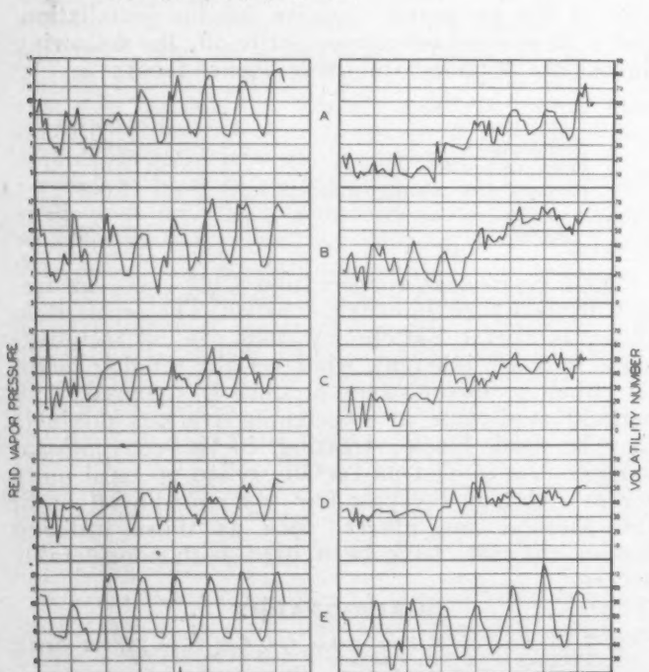


FIGURE 1
Volatility trends of a number of the major housebrand gasolines

The same survey data plus information secured since that time provides the background for the present paper. Figure 1 is an illustration of the volatility trends of a number of major motor fuels. The first 4 companies designated as A, B, C, and D, marketed approximately 40 percent of all the fuel sold in the 8 states of Arkansas, Colorado, Illinois, Indiana, Iowa, Kansas, Minnesota, and Missouri, during the 12 months ending October 31, 1934. Pronounced seasonal characteristics are apparent, particularly in the matter of vapor pressures. Increasing volatility and some tendency toward seasonal variation of volatility is apparent in the case of at least 3 of the first 4 fuels although the curves are admittedly somewhat irregular.

In Table I and Figure 2 a new method is used to present the ever changing picture of motor fuel quality. This method tends to smooth out the irregularities and strikingly illustrates the long-time trends. The data are the "yearly by months" averages for the same four companies previously referred to.

It will be noted that the vapor pressure has been steadily increasing at the rate of about a quarter of a pound a year. The mid-point volatility as measured by volatility numbers increased greatly during the period of 1932 through 1934. Since that time it has suffered little change and appears to be undergoing a temporary breathing spell. The butane content averages presented in the lower graph started out by being irregular. During 1933 and 1934 the butane content averaged about 5.7 percent. Since that time the butane content has increasd until at present it averages somewhat over 6 percent. The butane contents shown in this graph were arrived at by applying the graphic analytical method of Alden and

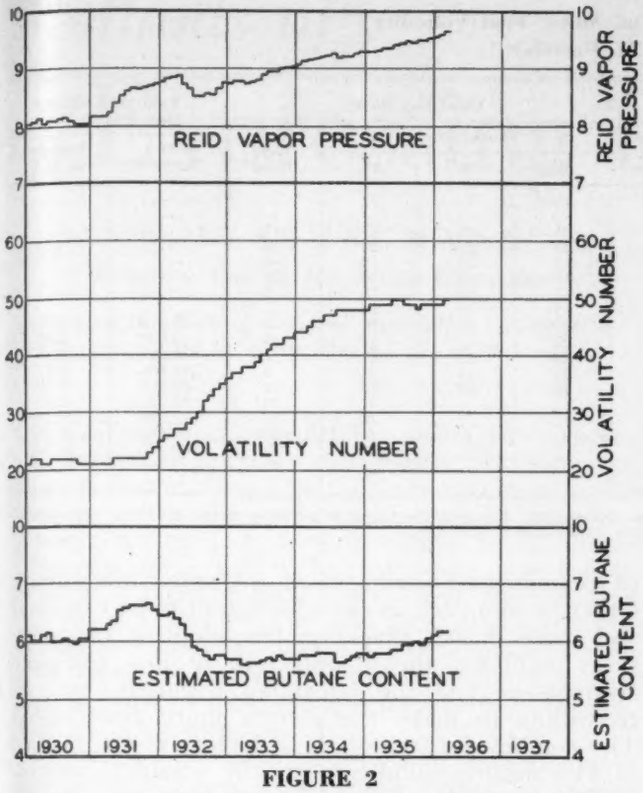


FIGURE 2

Average characteristics of several major motor fuels (yearly by months)

Blair[2]. These methods have been repeatedly checked against actual analyses for verification with excellent results.

When the three curves of vapor pressure, volatility number and butane content are examined simultaneously, a number of cases of inter-relationship are immediately obvious. The irregularities in the vapor pressures and butane contents prior to 1933 are probably traceable to failure on the part of refiners to effectively de-propanize their products. The drop in vapor pressure and in butane content which occurred in 1932 may be due to a sad awakening on the part of refiners, a realization that fuel systems of cars were unable to handle the new higher pressure fuels. The set-back, however, was only a temporary one. The steady increase in vapor pressure since the time of that temporary decrease is mute evidence that powerful economic forces within the oil industry over which gasoline manufacturers have little or no control are at work. It is the economic pressure of large volumes of butane endeavoring to reach a logical market outlet.

Returning to the subject of volatility we find that in the years 1933 and 1934 the vapor pressure was steadily increasing while the butane content remained substantially constant. It is obvious that the increased mid-point volatility is the answer for the increasing vapor pressure during this period. A little later on, through 1935, we find the mid-point volatility becoming constant but the vapor pressure is still increasing at about its normal rate. The answer for this is found in the butane content which was also gradually increasing.

NOTE: [2] "Economic Outlets for Natural Gasoline and Liquefied Petroleum Gases" Proceedings 13th Annual Meeting A.P.I., Houston, Texas, Nov. 16, 1932.

TABLE I

Average Characteristics of Several Major Motor Fuels Yearly By Months

Year	Month	R.V.P.	Vol. No.	Butane	Year	R.V.P.	Vol. No.	Butane
1929	December	8.14	21	6.20				
1930	January	8.05	21	6.10	1933	8.74	36	5.70
	February	8.06	22	6.00		8.78	37	5.70
	March	8.10	22	6.00		8.77	37	5 70
	April	8.02	21	6.10		8.75	38	5.60
	May	8.09	21	6.15		8.78	38	5.65
	June	8.07	22	6.00		8.80	39	5.65
	July	8.09	22	6.00		8.89	40	5.70
	August	8.11	22	6.05		8.93	41	5.70
	September	8.08	22	6.00		8.94	42	5.65
	October	8.02	22	5.95		9.01	42	5.75
	November	8.03	21	6.05		9.00	43	5.70
	December	8.03	21	6.05		9.01	43	5.70
1931	January	8.15	21	6.20	1934	9.08	44	5.70
	February	8.17	21	6.20		9.13	44	5.75
	March	8.14	21	6.20		9.15	45	5.75
	April	8.25	21	6.30		9.18	46	5.75
	May	8.39	22	6.35		9.20	46	5.80
	June	8.54	22	6.55		9.22	47	5.80
	July	8.61	22	6.60		9.23	47	5.80
	August	8.65	22	6.65		9.18	48	5.65
	September	8.64	22	6.65		9.20	48	5.65
	October	8.67	22	6.65		9.20	48	5.70
	November	8.70	23	6.65		9.24	48	5.75
	December	8.73	24	6.55		9.27	48	5.80
1932	January	8.76	25	6.45	1935	9.28	48	5.80
	February	8.82	26	6.45		9.27	49	5.75
	March	8.85	26	6.50		9.32	49	5.80
	April	8.86	27	6.40		9.34	49	5.80
	May	8.76	27	6.30		9.34	49	5.80
	June	8.64	28	6.10		9.42	50	5.85
	July	8.53	29	5.90		9.44	50	5.85
	August	8.53	30	5.85		9.45	49	5.95
	September	8.59	32	5.75		9.44	49	5.95
	October	8.58	33	5.70		9.46	48	6.00
	November	8.67	34	5.75		9.46	49	5.95
	December	8.75	35	5.75		9.50	49	6.05
1936	January				1936	9.55	49	6.10
	February					9.59	49	6.15
	March					9.62	50	6.15

Now that we have shown the trend in volatility characteristics it will be of interest to determine from whence this volatility comes. Vague statements have frequently been made during the past several years regarding the change in the relative volumes of natural and refinery vapor recovery gasolines. Again it is a changing picture upon which we believe some light can be thrown by applying our knowledge of blending. Therefore, let us start with the information we have avilable on volatility numbers and work backwards.

Volatility number as applied to motor fuels, by our definition, is the numerical difference between the observed 50 percent evaporated temperature and 284° F. which is the maximum mid-point temperature of U. S. motor specification gasoline. Since this maximum mid-point temperature of 284° F. represents the least volatile gasoline acceptable under the specifications, such gasoline is designated as having a volatility number of zero.

A survey of average gasolines as established by the Bureau of Mines reports shows that at no time since 1920 has the volatility number of motor fuel been as low as zero. It appears from these data that the lowest volatility ever offered occurred in 1925 during which year the average volatility number was 14. The quantity of natural gasoline produced in that year represented 9.79 percent of the total motor fuel. When this volume of light gasoline is deducted from the average fuel of that year it appears the volatility number of the refinery-produced gasoline was exactly zero. This gives us a logical starting point.

From 1925 on we are confronted with other factors

TABLE II

Effect of Natural Gasoline on Motor Fuel Volatility
(Quantities in M. Barrels)

YEAR	Total Production of:		Natural In M.F. Percent	Volatility Nos.				Volatile Refinery Gasoline in Base	
				Motor Fuel			Ref. Base		
	Motor Fuel	Natural Gasoline		W.	S.	Av.		M Barrels	Percent of M.F.
1918	90,556	6,727	7.42	..	..	..	..	.....	....
1919	101,145	8,370	8.28	..	..	..	..	.....	....
1920	124,030	9,161	7.39	25	16	21	11	.....	....
1921	132,248	10,713	8.10	23	22	23	12	.....	....
1922	157,742	12,044	7.64	17	14	16	6	.....	....
1923	194,977	19,434	9.97	17	15	16	3	.....	....
1924	223,018	22,235	9.97	17	13	15	2	.....	....
1925	268,667	26,307	9.79	18	9	14	..	.....	....
1926	306,605	32,305	10.54	20	18	19	5	10,472	3.58
1927	339,910	38,657	11.37	20	17	19	4	9,038	2.66
1928	387,722	42,326	10.92	23	19	21	7	16,579	4.28
1929	444,859	52,271	11.75	21	21	21	5	15,704	3.53
1930	444,391	52,631	11.84	28	24	26	12	33,300	7.49
1931	441,837	43,617	9.87	..	..	31	20	55,751	12.62
1932	403,603	36,281	8.99	..	..	40	31	77,138	19.11
1933	411,706	33,610	8.16	..	..	46	39	94,524	22.96
1934	427,034	36,556	8.56	..	..	50	42	103,477	24.23
1935	465,514	38,858	8.35	..	..	50	42	113,064	24.29

Notes: Production figures from A.P.I. Statistical Bulletin, May 1934. Volatility Nos. 1920 to 1930, Inc. from Bureau of Mines Semi-annual Surveys. 1935 Production data from Bureau of Mines Preliminary Statement included in December 1935 monthly Statement.

in addition to natural gasoline which contribute to motor fuel volatility. Of these factors vapor recovery gasoline is probably the most important. At the beginning of 1925 oil cracking processes were accounting for about 25 percent of the motor fuel production. Refinery vapors which up to that time had been largely wasted or used for fuel gas were beginning to be processed for the recovery of light gasolines similar to natural gasoline. The increasing quantities of light gasolines recovered from refinery vapors cannot be very accurately established due to its immediate absorption in the motor fuel stream. Other factors such as the adoption of more extensive and more drastic cracking, the adoption of operations involving the manufacture of low end-point straight-run and the reforming naphthas, etc., all contribute to make the picture more complicated. The combined effect of these factors is an increase of 42 volatility numbers, i.e., the volatility number of refinery produced gasoline rose from zero in 1925 to 42 in 1935. The volume of light refinery gasoline of the vapor recovery type necessary to effect a change of that magnitude can readily be calculated.

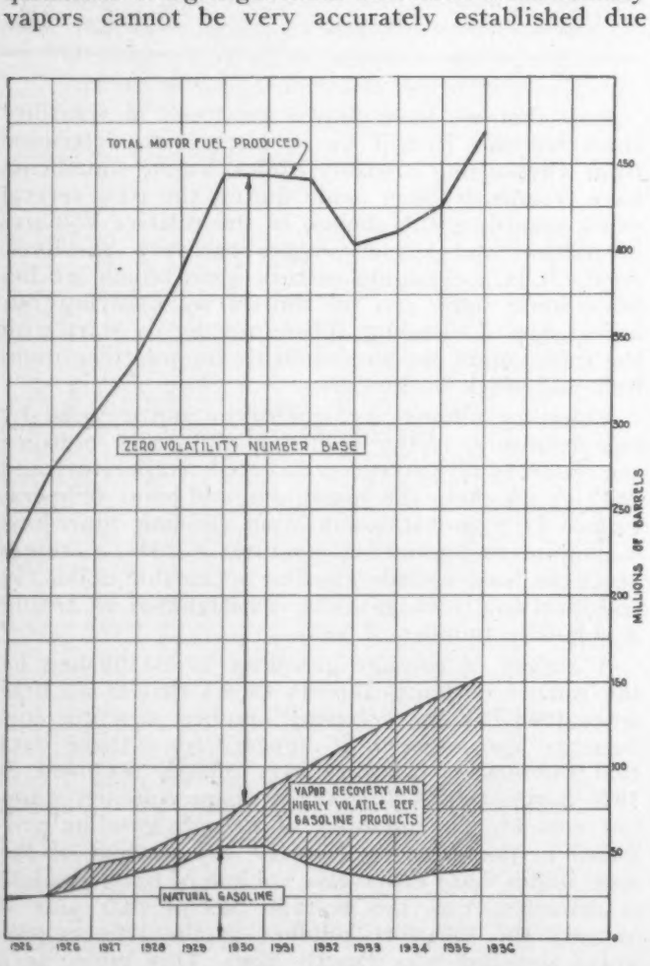


FIGURE 3
Natural gasoline and volatile refinery products in motor fuel

Thus, if it is assumed that the heavy refinery base of 1935 was still a zero volatility number product such as we had in 1925, it would have required 113,064,000 barrels of a product similar in character to natural gasoline to produce the quality of that year's refinery gasoline. The addition of the 38,858,000 barrels of natural produced in that year served to further increase the volatility number from 42 to 50. Table II shows the relative amounts of natural and vapor recovery gasoline for the last 10-year period. The same information is presented graphically in Figure 3. It will be noted that approximately three quarters of the light gasoline which supplied the motor fuel volatility of 1935 was produced in the refineries. This is almost the exact reverse of the situation in 1926 when the bulk of the volatility was supplied by natural gasoline.

The changing picture of fuel volatility as to source and as to volumes has been accompanied by a marked change in the objectives of our industry. In 1926 we were chiefly interested in fitting fuels to engines. Today our objective is to see that new engines are properly fitted to today's and tomorrow's gasoline, and not to yesterday's gasoline. Colder manifolds and cooler carburetors will be necessary to take the most of this new gasoline. Some of us may be inclined to harbor fears for the future of volatility but such things have a happy way of taking care of themselves. It should be remembered that every step taken by automotive manufacturers to remove heat from the induction systems not only makes the more volatile fuels desirable but compels the marketers to supply more volatile products.

The writer wishes to acknowledge the helpful assistance of M. G. Blair in preparing the tables and charts for this paper.

Methods of

Expressing the Volatilily of Motor Gasolines

W. W. SCHEUMANN
Empire Oil & Refining Company

Before the Natural Gasoline Association of America held in Tulsa, May 13-15, 1936

THAT satisfactory volatility should be considered the most important characteristic of motor gasolines is evident, from a practical observation, to anyone who has ever had to start a cold automobile motor on a sub-zero morning, or drive that same car in western Oklahoma on a typical July afternoon. Lacking the benefits of these practical observations, the same conclusions will be reached by even a casual perusal of the literature covering the relationship of automobile engine performance and motor fuel characteristics. Here is at least one case of complete agreement between the practical and the theoretical.

However, if the question concerning the definition of volatility is raised, or a satisfactory method for expressing such volatility requested, then all this complete harmony of thought disappears and we find not only various methods advocated for the expression of volatility, but we find that the concept of volatility itself varies widely and is often used in a misleading or incorrect manner.

Brown[1] states that motor fuel volatility may be defined as the degree to which a fuel will vaporize under specified equilibrium conditions. The Standard dictionary gives the following definitions:

1. Volatility, the state or quality of being volatile. 2. Volatile. (a) evaporating rapidly at ordinary temperatures on exposure to the air, as i.e., volatile oils. (b) capable of being vaporized. 3. Volatilize, to cause to pass off in vapor.

A consideration of these definitions would indicate that volatility as referred to motor fuels is a quality of the fuel which indicates its ability to vaporize, or the degree to which it will vaporize, at specified temperature conditions and ratios of air to fuel.

EARLY CONCEPTS OF VOLATILITY

The first demonstration of a gasoline engine-powered vehicle is generally attributed to Elwood Haynes in 1894, at which time gasoline was simply a by-product of little value, produced chiefly from the distillation of Appalachian crudes. However, the automobile industry proved to be a lusty infant, and soon the increasing production of cars caused a simultaneous increase in the demand for gasoline, so that the by-product developed into the major product of the petroleum industry. During this time volatility and all other properties of gasoline as well were governed solely by density or Baume gravity. While various gradations were made, all petroleum distillates above 60 degrees Baume gravity were usually called gasoline or naphtha. This type of gasoline led to many difficulties, such as poor engine starting, smoking of exhaust, carbon deposition, lack of uniform performance, and there existed, therefore, almost universal agreement that a better method of quality control was necessary. The result was the development of the distillation test method. Many individuals and organizations too numerous to mention herein assisted in this development; however, by 1915 the American Society for Testing Materials had proposed a standardized method of test, and the first standardized specifications for gasolines were issued by the United States Fuel Administration in 1918, the apparatus and methods of test being published in United States Bureau of Mines Bulletin 166[2].

The general adoption of this distillation test method did make possible the production of more uniform gasolines. However, there did not exist any background of facts relating the results of these tests and the volatility of the fuel in an engine, and many acrimonius discussions occurred as a result, regarding the relative importance of gravity or "initial" and "end point." Generally, it was assumed that the end point of a fuel represented or designated its volatility, and that the initial boiling point designated in some manner engine starting characteristics. Both of these ideas were subsequently proved to be incorrect.

EARLY WORK ON FUEL VOLATILITY

By the early part of the 1920's the Engler distillation had become the subject of considerable attack from the technically minded regarding its suitability as the satisfactory means for the determination of gasoline volatility. This was largely due to the fact that it was recognized that the test is a batch affair, involving a certain amount of fractionation, that it completely neglected from 1 to 5 percent of very light fractions which were lost during the test, that because as distillation proceeded the character of the residue in the flask became increasingly different from anything produced under engine conditions, and because the end point of the distillation is nearly 300° F. higher than the temperature of complete vaporization in the engine manifold.

As a result of this variation of ideas, research on the question of fuel volatility was not only greatly stimulated in the various larger laboratories of the petroleum and automotive industries, but resulted in the formation in 1922 of the Cooperative Fuel Research Steering Committee, representing both of these groups and the National Bureau of Standards. One of the first undertakings of this organization was a study of the effect of fuel volatility on engine performance. Similar work was also done by other agencies, notably the Natural Gasoline Association of America, whose research program on motor fuels was carried out by Dr. George G. Brown at the University of Michigan. As a result of these investigations, ideas regarding the effect of motor fuel volatility have been greatly clarified, and it is now possible to state with some confidence the fuel properties required for a given condition of engine operation. Moreover, the value of the simple and rapid distillation test method was also greatly enhanced by this work due

to the establishment of an interpretation of results based on experimental facts.

This work was carried out largely during the years 1922 to 1930 and is of such magnitude that it cannot be reviewed here in any detail. Moreover, the literature on the subject of relating true fuel volatility as measured by various intricate means with engine performance and the correlation of this with the distillation test is so extensive that it would be most difficult to even attempt to give proper credit to the various investigators. The same is also true of the relationship of vapor pressure of fuels and vapor-locking tendencies in automobiles, and therefore direct references have been omitted in the following paragraphs briefly summarizing these findings.

Volatility of motor fuels, when related to engine performance, is not a single property, but the volatility of different portions of the fuel is of importance for different reasons.

The engine starting properties of fuels are intimately related to their A.S.T.M. front end distillation characteristics, and it is generally agreed that on the average the 10-percent point on the A.S.T.M. distillation curve, corrected for loss, is the best available indication of the average ease of starting of a given gasoline. Therefore, if the engine temperature and air-fuel mixture supplied by the carburetor (with choke on) are defined, the 10 percent fuel value necessary for easy starting can be closely estimated. Brown[3] states that this average relation may be expressed as follows:

Easy Starting.—Ten percent evaporated temperature must be less than 1.25 (100 + engine temeparture, °F).

The middle portion of the A.S.T.M. distillation curve is related to the ease of warming up an engine and the accelerating characteristics, although this relationship is considerably more complex than that previously discussed. Manifold and carburetor details, as well as air-fuel ratios, affect the relationships involved but as an overall average Brown[3] states the following:

Satisfactory Warming Up.—A.S.T.M. 35 percent evaporated temperature must be less than (100 + 1.5 mixture temperature, °F.).

Good Acceleration, Driving Conditions.—A.S.T.M. 60 percent evaporated temperature must be less than (2 × mixture temperature, °F.).

VAPOR LOCK

The temperature of complete vaporization and the tendency toward crankcase dilution are both related to the 90 percent point on the A.S.T.M. distillation curve. From this value may be calculated the dew point and hence the temperature at which a dry mixture of fuel and air may be formed for any given air-fuel ratio. Abnormally high values tend to promote crankcase dilution. The significance of this factor is probably not as important as those previously discussed.

One other operating characteristic which bears a relation to fuel volatility is vapor lock. Vapor lock occurs when the fuel boils excessively in any part of the fuel system as the result of being heated to such a temperature so that the vapor pressure exceeds atmospheric. It has been found that this temperature is approximately equal to the 10 percent evaporated value of the distillation curve. A more satisfactory method for measurement of this tendency, however, is the direct determination of vapor pressure as usually carried out by the Reid method. Voluminous data have been published correlating vapor pressure and the occurrence of vapor lock in automobiles.

As a result of all this the volatility characteristics of motor gasolines can be correctly specified and rendered suitable for any usual engine operating condition by proper choice and control of the 10, 35, 60 and 90 percent distillation points and the vapor pressure. In fact, a study of many specifications will indicate that these control points are being used today in conjunction with weather statistics to establish proper seasoned gradation of volatility.

VOLATILITY INDEX

In spite of the fact that this method of control is neither complicated in application nor difficult of comprehension, it lacks sales appeal, and there has existed for some time a considerable demand for a still more simplified method of expressing volatility, one which, if possible, would utilize only a single term or number. It is argued that a single index of gasoline volatility would be highly acceptable to the trade in general, as there exists a natural tendency to favor a single number classification over one where the mental effort must be carried out of weighing two or more values against each other. The general adoption of such a term would therefore be a new source of inspiration to advertising departments and would make for more effective sales talks. Other arguments advanced are that it would assist the automobile builder in the design of cars, would simplify state laws and specifications, and would aid in the establishment of seasonal volatility control.

The use of such an index would require the making of several assumptions; however, in this very fact lies perhaps one of the best arguments in its favor. A general interpretation of the A.S.T.M. distillation test requires that certain assumptions regarding engine temperatures, air-fuel ratios, certain carburetor and manifold characteristics, and other features be made. Therefore, the actual accuracy may be but slightly impaired if several additional assumptions are made, as has been done in some of the following methods proposed for a simplified volatility index.

One of the earliest methods of indexing volatility was the use of the average boiling point. The Bureau of Mines has made use of this value as an expression of overall volatility, in their gasoline surveys. It was calculated by adding the initial boiling point, the maximum boiling pont, and each of the 10 percent distillation points and dividing the sum by 11[4]. This index assigns equal importance to all points on the distillation curve, which is not true, and it is therefore not desirable as an expression for volatility as related to engine performance.

Brooks and Bruce[5] have suggested a volatility index indicative of the effect of volatility on acceleration. They suggest the use of varying points on the A.S.T.M. distillation curve as key points, depending upon the mixture temperatures. For example, at 32° F. mixture temperature the 5 percent evaporated point is the key point and at 212° F. mixture temperature the 80 percent point is the key point. Under usual operating conditions, mixture temperatures are in the neighborhood of 150° F. to 160° F. and this system would therefore suggest that gasolines be judged for accelerating characteristics from a comparison of their 55 or 60 percent distillation points, increased effectiveness being indicated by an increase in the reciprocal of the absolute temperature of the key point.

A much simpler proposal, serving about the same purpose, is that of Oberfell and Alden[6]. They point out that practically all commercial gasolines have 10 percent distillation values sufficiently low for satisfactory starting and 90 percent distillation values which are entirely permissible for satisfactory performance, but that the

greatest variations occur in the middle portion of the distillation curve which governs the warm-up period. They suggest, therefore, that this characteristic be expressed in a volatility index which is calculated by the following equation:

Volatility index = 284 — 50% evaporated temperature, °F.

This index can be simply calculated and does offer a means of comparing average relative warming up characteristics of fuels. It gives a good spread of values, United States motor gasoline being zero on this scale and fighting grade aviation gasoline about 72. This index is more or less an abstract number and no correction for atmospheric or mixture temperatues is included.

A somewhat similar index has been suggested by Hebl and Rendel[7]. They also discard the question of starting and point out that a fuel of satisfactory warming up characteristics is almost always satisfactory in starting characteristics. Their warming-up index is calculated from the 20 and 70 percent evaporated distillation points by means of an alignment chart which the authors have developed. However, they also recognize the effect of the test temperature on the warming-up period and have therefore prepared a temperature correction which is applied to the distillation results. Their volatility index as a measure of warming-up quality depends, therefore, upon the 20 and 70 percent evaporated points and the atmospheric temperature.

This index in some respects is probably nearer technically correct than that of Oberfell and Alden. However, its determination is somewhat more complicated, which is undesirable, since a primary requisite for such an index is extreme simplicity. The question of temperature correction is, however, a vital one. It is perfectly true that the degree of volatility necessary to give a specified warming up performance differs with operating temperatures. However, whether or not this factor should be included in a volatility index is debatable. From one angle it would seem to be more desirable to keep such an index as abstract as possible, and recognize the desirability of different index values for seasonal conditions. However, through the activities of many marketers of petroleum products the general public has been educated to believe that improved quality is synonymous with increased numerical values for indices of various sorts. The case of octane numbers and viscosity indices of lubricating oils may be offered as examples of such public education. The present-day car, however, cannot, in many cases, digest highly volatile gasolines in hot summer weather, particularly if such gasolines have a high vapor pressure. The general use of such an abstract index, therefore, would require that one of three things be done. Either the public would require educating to the fact that the most desirable volatility index should vary with the season, or the producer of motor fuels would be forced to excessive removal of butanes from his product in order to produce a high volatility index, low vapor-pressure gasoline during the summer season, or as a third possibility, the automobile builder would be forced to build cars which could operate satisfactorily on high vapor pressure gasoline in hot weather, although this would offer little relief to cars now in operation. Therefore, the use of an index which would give identical numerical values with gasolines of varying volatility at corresponding atmospheric temperatures has much to be said in its favor.

In this connection, a paper presented by Eisinger and Barnard[8] before the June, 1935, meeting of the S.A.E. is of interest. These investigators studied the effect of partial volatility of fuels as represented by the percent evaporated at 158°F. and the effect of total volatility of fuels as represented by the 90 percent point on automobile acceleration with various intake manifold temperatures. They found that both of these factors were of importance, improved acceleration being made possible by either increasing the percent evaporated at 158°F. or by lowering the 90 percent temperature. Moreover, identical performance could be obtained by either method, as increasing the percent at 158°F. by 1 percent was approximately equivalent to lowering the 90 percent value by 5°F.

While they do not propose a volatility index based on these values, their data substantiate the claim of Hebl and Rendel that a suitable volatility index should be based on points taken from both the lower and upper parts of the distillation curve. However, it can also be argued that the 50 percent point averages the amount evaporated at 158°F. and the 90 percent temperature and therefore if it is admitted that the index based on this value is only approximately accurate this argument holds good.

CONCLUSION

At the present time the A.S.T.M. distillation test can be interpreted in terms of engine performance, and when coupled with the vapor pressure test gasolines can be designed for any particular or general service. While these test methods serve admirably the purpose of the refiner and the automotive engineer, they are perhaps too complicated for presentation to the general public, and as a result the story of volatility has not been as widely told as is possible. Considerable demand, therefore, exists for a simplified volatility index which might summarize in a suitable manner the results of these other tests. Such an index would make possible the emphasizing of volatility and would primarily be of service to advertising and sales activities.

Several methods of deriving an index of this type have been proposed. They relate chiefly to the middle portion of the distillation curve and, as such, to warming-up periods and acceleration in engine performance. There are, however, several factors on which complete agreement does not exist. One of these is the relative necessity for the use of one or two points on the distillation curve. It would appear that the use of one point, such as the 50 percent value, would be preferable for the sake of simplicity and would probably be of the same degree of average accuracy as the use of several points. The second factor is the need of a method for temperature correction. This should be developed so that desirable index values can be maintained in hot weather without producing a product having excessive vapor-locking tendencies in present day cars.

If these factors are properly handled, a volatility index can be evolved which would serve a decidedly useful purpose in presenting a correct story of volatility to the general driving public.

REFERENCES

[1] Brown, George G., The Relation of Motor Fuel Characteristics to Engine Performance, Eng. Res. Bulletin No. 7, University of Michigan.

[2] Francis, C. K., Development of Gasoline Specifications, The Oil and Gas Journal, 30 (23) 30 (1931), October 22.

[3] Brown, George G., The Volatility of Motor Fuels, Eng. Res. Bulletin No. 14, University of Michigan.

[4] Hill and Dean, Bulletin 191 (1920), U. S. Bureau of Mines.

[5] Brooks and Bruce, S.A.E. Journal, 26, 474 (1930).

[6] Oberfell, G. G., and Alden, R. C., Suggest Volatility Index for Motor Fuels as Aid in the Utilization of Light Hydrocarbons, The Oil and Gas Journal, 31 (35) 14 (1933), January 10.

[7] Hebl, L. E., and Rendel, T. B., The Importance of Correct Volatility for Winter Car Performance, Proceedings 14th Annual Meeting, Natural Gasoline Association of America (1935), pp. 31-36.

[8] Eisinger, J. O., and Barnard, D. P., Effect of Gasoline Volatility Changes on Automobile Road Performance, The Oil and Gas Journal, 34 (8) 34-39 (1935), July 11.

The Spectacular Side of Hydrocarbons

DR. SIDNEY BORN
Director of Petroleum Research
University of Tulsa

Before the Natural Gasoline Association of America, Tulsa, May 14, 1936

FOR some years the natural gasoline industry has been greatly interested in finding new markets for its products. There was a time when the manufacturers of gasoline were satisfied with the market afforded by the motor fuel industry. Although the natural gasoline industry dates back hardly more than a quarter of a century, attempts to find other uses for the products contained in natural gasoline were initiated as early as 1914.

The chemical industries of the United States cover such a vast field that they affect every phase of our daily life. The food we eat is raised with the aid of chemical fertilizer. The clothes we wear are prepared with the aid of many chemical substances; they are colored with synthetic dyes, and in some cases—as artificial silk and rayon—are in themselves chemical products. The stem of the pipe in which you smoke your tobacco is a chemical product and has probably been made partly from natural gas. It may seem strange that a material as solid as your pipe stem can be made from an almost intangible material like gas.

Natural gasoline is composed almost entirely of paraffin hydrocarbons, ranging from propane to decane or even higher in some cases. Natural gas itself may have all these hydrocarbons and in addition methane and ethane.

In considering raw materials for any manufacturing purpose, cost is a prime consideration. Two of the most widely used chemicals for industrial purposes are salt and sulfuric acid. Salt sells for about $8 a ton and sulfuric acid for about $16 a ton. Let us consider for a moment how the cost of natural gas compares with these products. One thousand cubic feet of natural gas weighs approximately 50 pounds and if natural gas is figured at 10 cents per 1000 cubic feet, this will make a ton of natural gas cost approximately $4, so we have as a raw material a very cheap product.

REACTIVITY

The next consideration in choosing a raw material for use in our chemical industries is reactivity; that is, the substance must be capable of reacting with various reagents to form new substances and must be capable of forming new materials under the influence of heat and pressure. The hydrocarbons found in natural gas are substances from this standpoint.

Among the first chemical substances to be synthesized from natural gasoline was amyl acetate. There was a great demand for amyl acetate during the World War as this substance was needed in the manufacture of explosives. Until the World War this material was manufactured from amyl alcohol and acetic acid, both products of natural fermentations.

On account of a great shortage, American chemists were faced with the necessity of finding a new source of raw material for this substance. They found such a raw material in the pentane fraction of natural gasoline. It is a comparatively simple thing to fractionate natural gasoline and isolate the pentane. The pentane is then subjected to the action of chlorine gas under fixed conditions, until a predetermined amount of chlorine has been absorbed. The products formed by this reaction are then washed and redistilled to recover a product known as amyl chloride, which is pentane in which one hydrogen atom has been displaced by chlorine. The amyl chloride is heated with sodium acetate under pressure, resulting in the production of amyl acetate. Not only is amyl acetate widely used in the explosive industry, but it is also used as a solvent in the manufacture of artificial silks, celluloid, photographic films, imitation leathers and the manufacture of quick-drying lacquers and paints. Some of you may be familiar with this substance under the more common name of "banana oil."

Another interesting development has been the manufacture of ethylene glycol from ethylene and chlorine gas. A plant for the manufacture of this substance has been in operation for years by Carbide & Carbon Chemical Corporation. This material has been used in the preparation of anti-freeze compounds for automobile radiators. Ethylene glycol is also used as a solvent in the manufacture of concentrated fruit flavors, flavoring extracts, and similar commodities. It is used in the manufacture of cosmetics, in the treatment of skins and furs, in the moistening of tobacco, in the leather industry, and in the textile industry in the treating and finishing of fabrics. Some of the esters and ethers of ethylene glycol are widely used in the chemical industry as solvents for cellulose nitrate, gums, shellacs, etc. Other compounds are used in the preparation of lacquers, wetting, cleansing and emulsifying agents.

ARTIFICIAL RUBBER

Other chlorinated derivatives of the olefins have been manufactured for years and have been used extensively in the manufacture of rubber goods.

For years the creation of artificial rubber has claimed the attention of chemists. Natural rubber is made from a sticky, milky fluid, called latex, which is found between the inner wood and the outer bark of the rubber tree. When the latex is mixed with a suitable coagulant the rubber separates out as a light doughy mass which is the raw material from which most of our rubber goods have been manufactured.

About 15 years ago a chemist in Kansas City was attempting to produce a new anti-freeze for automobile radiators. In his experiments he mixed some ethylene dichloride and sodium polysulfide. Instead of obtaining the clear-looking liquid he was expecting, he obtained a mass which looked and felt and behaved like rubber.

From this interesting beginning developed the first synthetic commercial rubber produced in the United States. The product developed in this manner is sold under the name of "thiokol" and while it is not exactly the same as natural rubber, yet many products manufactured therefrom are more suitable for their purpose than the natural rubber would be.

Among the things made from this material are rubber hose for gasoline and oil; hose for lacquer sprays; rollers for printing-presses; and for such purposes it is superior to natural rubber.

The Dupont Company has also developed an artificial rubber which, for many purposes, is superior to natural rubber. That is, the product is more resistant to oxidation and to chemical actions. This material is sold under the trade name of "Duprene" and is made from acetylene. The acetylene is first changed to vinyl acetylene and then, by the addition of hydrochloric acid to chloroprene, which is then polymerized to a synthetic, rubber-like substance.

ALCOHOLS

The reaction between ethylene and sulfuric acid was understood as early as 1821 by Hennel, who pointed out that alcohol or ether could be produced by this reaction. Nothing seems to have been done, however, until Fritsche, in 1900, built a plant near Richmond, Virginia, where ether was commercially produced from oil gas until 1907 when the removal of the revenue tax from industrial alcohol permitted the production of ether from alcohol at a cost below that at which it could be profitably manufactured from oil gas. This price factor, however, would not hold true if the oil gas were a by-product of a cracking operation.

Similarly, higher alcohols and their esters can be produced from other, unsaturated hydrocarbons by the action of sulfuric acid, and subsequent hydrolysis. A pilot plant for carrying out these reactions was constructed under the writer's direction in Okmulgee about 18 years ago. The process now is being carried out commercially by Standard Oil Development Company for the production of these higher alcohols.

When natural gas is burned with a sufficient supply of air the reaction products consist of carbon dioxide and water, but if the supply of air is restricted and the conditions controlled many different reaction products may be obtained, such as formaldehyde, methyl alcohol, acetylene, and unsaturated hydrocarbons. Possibly some of you have noticed the peculiar odor arising when a gas burner blows back and combustion takes place at the base of the burner with an insufficient air supply. A great deal of work has been done on this problem and numerous patents have been granted on variations of this general reaction. A plant has been in operation for some time in Oklahoma in which natural gas is mixed with air and carbon dioxide and heated to a temperature of 800 to 900° F. in the presence of a catalyst. This catalyst may consist of platinum, palladium, copper, chromium, manganese, iron, nickel or the oxides of these substances. Pressure ranging from 100 to 300 pounds is employed, and formaldehyde and methyl alcohol are obtained in commercial quantities by this reaction. Formaldehyde is used for the production of synthetic resins, and methyl alcohol is largely used as an anti-freeze in automobile radiators.

It is possible to point out to you only a few of the many substances that can be manufactured from the hydrocarbons present in natural gas and natural gasoline. Thousands of different materials may be produced synthetically from these raw materials. Even to give a list of the products that are being made and can be made would probably require several hours.

It seems to me that we have barely scratched the surface of a mine whose hidden treasures are so vast in extent that it is almost impossible completely to visualize them.

There is not a single field of commercial enterprise in which it will not play a role. Great credit is due to the men of vision and the men of courage who have pioneered this work. In an industry whose background dates back not over 25 years the work has just been started. Much development, research and painstaking effort must be expended to carry it on. To those who succeed the reward should be very rich indeed.

Polymerization of Gases to Produce Gasoline

C. R. WAGNER
The Pure Oil Company

Presented before the joint conference of Pennsylvania Natural Gas Men's Association with the Sixth Pennsylvania Mineral Industries Conference, Pennsylvania State College.

THE existence of large quantities of olefinic gases produced by high temperature cracking processes during the last decade has been the impelling factor behind the development of current polymerization processes. By no stretch of the imagination could such huge volumes of olefines be absorbed by the chemical industry. As a conservation measure, to reduce the rate of exhaustion of our crude oil reserves, and as a means of producing a high octane value blending fuel polymerization is well justified.

There are today three polymerization processes available to the public: 1. The thermal process developed by Phillips Petroleum Company. 2. The catalytic process of Universal Oil Products Company. 3. The thermal process of The Pure Oil Company.

Phillips Petroleum Company has a plant operating at

Borger, Texas, processing, it is understood, a natural gas fraction consisting essentially of butanes. Pressures of 1000 to 3000 pounds per square inch are employed at temperatures of 950° to 1100°F. Characteristics of the product as reported by Keith[1] are as follows:

Product from Commercial Plant on Butane Feed (Clay treated)

A.P.I. Gravity	61.4	50%	180
ASTM Distillation	....	60%	203
°F. Initial b.p.	95	70%	229
5%	114	80%	271
10%	120	90%	361
20%	133	95%	425
30%	147	End pt.	449
40%	163	ASTM octane	79

Phosphoric anhydride, suitably supported in pellet form, is the catalyst used by Universal Oil Products Company in a process now installed in several plants. This process operates at pressures of about 200 pounds per square inch and at temperatures of the order of 400° to 500°F. The product produced consists almost entirely of olefines and usually it is deficient in fractions boiling below 158° F. Very little polymer heavier than gasoline is made, however, and the raw product can be hydrogenated to produce a very high octane fuel. Commercial quantities of crude iso-octane (2,2,4-trimethylpentane) made in this manner are now being offered by at least two major companies. The following characteristics are reported by Egloff[2] for this type of polymer:

	Regular Polymer	Selective Polymer (di-isobutane)	Hydrogenated Selective Polymer
A.P.I. Gravity	67.0	64.5	71.0
ASTM Distillation Initial boiling pt.	101	212	206
10%	156	213	208
20%	178	214	209
50%	212	215	210
90%	314	216	213
End point	408	238	244
ASTM octane number	83	84	99

In The Pure Oil Company process conditions are modified to suit the character of the charging stock available and the nature of the product desired. Any gases consisting of hydrocarbons having two or more carbon atoms per molecule may be used as charging stock, and a variety of products ranging from pure aromatics to material resembling vapor phase cracked distillate may be obtained. It is preferred, however, that paraffins be cracked in one stage and that olefines be polymerized in a separate stage, using in each step those conditions best designed to secure the desired results.

Two plants have been constructed and operated over the period of the last 5 years: one a semi-commercial plant producing about 100 barrels of gasoline per day, the other a larger unit producing about 500 barrels per day. A third plant was erected abroad about 3 years ago, but operating data have been withheld since the plant is government property.

The small plant just referred to has operated on a variety of gases ranging between straight absorber exit gas as one extreme and stabilizer reflux as the other. Analyses of the two gases are shown below:

	Absorber Gas	Stabilizer Reflux
Methane, hydrogen, etc.	38	4
Ethylene	25	2
Ethane	14	—
Propylene	17	27
Propane	3	—
C^4 compounds	3	67
Specific gravity	0.99	1.50

Without pyrolysis of the paraffins present yields of gasoline as high as 3.25 gallons per thousand cubic feet were obtained on the absorber gas and as much as 9.0 gallons per thousand from the stabilizer reflux. These yields could be increased materially by decomposing the paraffins and then polymerizing the olefins so produced.

In the larger plant mentioned the feed stock was prepared by concentrating the olefins by means of absorption and redistillation under pressure. This charging stock was then delivered as a liquid to the poly furnace, where it was heated under pressure to reacting temperatures and then delivered to the reaction coil. The heat generated by the reaction caused a further rise in temperature of about 50° F. and this temperature was controlled by circulating air over the coil.

The characteristics of the products produced in these two plants are given in Table 1.

TABLE 1

	Raw Distillate		Finished Gasoline	
	Small Plant	Large Plant	Small Plant	Large Plant
Gravity, A.P.I.	54.0	57.3	57.0	58.5
Initial	84	85	90	92
10%	109	124	127	120
20%	135	151	145	148
50%	207	211	200	206
80%	325	329	281	335
End point 90% @	418	438	398	395
ASTM octane No.	...	75	77	79

A very interesting fact discovered early in this work was that aromatic hydrocarbons could be produced by polymerization of olefinic gases at much lower temperatures than by pyrolysis of paraffinic gases or gas oils. Operating at a temperature of 1175° to 1225° F. a product was obtained which had an A.P.I. gravity of 20 to 25 and which contained 75 to 80 percent of 400° F. end point distillate. This gasoline boiling point material had an A.P.I. gravity of 31 to 33 and, after acid treating to remove diolefines present, practically pure benzine, toluene, xylene, and naphthalene were separated by fractionation. Several hundred barrels of such material have been produced and the installation of a commercial-sized unit is under consideration.

	Raw Condensate	Gasoline Fraction
Gravity	25.1	32.9
Initial	90	148
10%	178	180
20%	185	190
50%	258	220
70%	354	254
90%	—	348
End point 73% @	418	413
Octane No.	—	99

It has been reported that it is possible to convert 90 percent or more of a paraffin gas, such as propane, into the corresponding olefine by means of suitable dehydrogenating catalysts. With yields for the polymerization step varying from 75 to 90 percent, depending upon the product desired and the process used, it is easy to see what a tremendous force may be exerted upon the fuel supply of the country and its cost to the public. Conservative estimates on the possible poly gasoline producible from refinery and natural gases indicate at least 4,500,000,000 gallons per year or more than 25 percent of the total gasoline consumed in the United States.

[1] Keith and Ward, 16th meeting, American Petroleum Institute, Los Angeles, Calif., Nov. 12, 1935.

[2] Egloff, Gustav, Kansas City Meeting, Petroleum Division, American Chemical Society, April 13-17, 1936.